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*May-June 1958*

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## OF THE USSR

(DOKLADY AKADEMII NAUK SSSR)

### Chemistry Section

IN ENGLISH TRANSLATION

*CONSULTANTS BUREAU, INC.*

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# CONTENTS

# CONTENTS (continued)

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# CARNALLITE AND SYNGENITE IN THE DEPOSITS OF THE DZHAKSY-KLYCH SALT LAKE (NEAR THE ARAL SEA)

I. N. Lepeshkov and Kh. B. Fradkina

(Presented by Academician I. I. Cherniaev, November 1, 1957)

Potassium-containing minerals are very rarely found in deposits of present day salt lakes.

G. G. Urazov et al. noted the presence of carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) and kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$) in the salt deposits on the shores of the Kara-Bogaz-Gola zone.

In a physicochemical investigation of the salt lakes on the northeastern shores of the Aral Sea, we found syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$) and carnallite in the deposits of the Dzhaksy-Klych Salt Lake

This lake is 20 km northeast of the Aral Sea. Besides the brine in the lake, there are deposits of salt in the form of astrakanite ($Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$), mirabilite ($Na_2SO_4 \cdot 10H_2O$), thenardite ($Na_2SO_4$), hydrates of magnesium sulfate ($MgSO_4 \cdot 7H_2O$, $MgSO_4 \cdot 6H_2O$, $MgSO_4 \cdot 5H_2O$, $MgSO_4 \cdot H_2O$), glauberite ($Na_2SO_4 \cdot CaSO_4$) and gypsum ($CaSO_4 \cdot 2H_2O$).

The total thickness of the strata in the lake is 4.5-5 m.[1].

There is a stratum of astrakanite (up to 1.5 m thick) and, in some regions of the lake, mirabilite and thenardite under the upper layer of sodium chloride (up to 2 m thick).

Crystals of magnesium sulfate hydrates (hexa-, penta- and monohydrates) and gypsum are found in the lower layer of the astrakanite stratum.

In the druses of astrakanite crystals we found syngenite in the form of fine, white crystalline inclusions of the following chemical and mineralogical composition (Table 1).

TABLE 1

| Salt | Content weight % | Mineral | Content, weight % |
|---|---|---|---|
| $CaSO_4$ | 9.27 | Syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$) | 33.72 |
| $MgSO_4$ | 24.85 | Astrakanite ($Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$) | 42.97 |
| $Na_2SO_4$ | 18.25 | Pentahydrate $MgSO_4 \cdot 5H_2O$ | 16.39 |
| $K_2SO_4$ | 17.89 | NaCl | 2.83 |
| NaCl | 2.83 | Water-insoluble residue | 4.40 |
| Water-insoluble residue | 9.11* | | |
| Σ . . . | 82.19 | Σ . . . | 100.31 |

* 4.71% $CaSO_4$ was taken from the insoluble residue of syngenite.

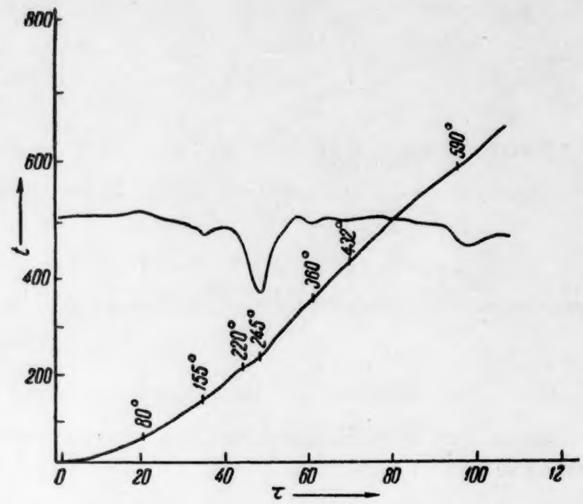


Fig. 1. Heating curve of syngenite.

The presence of syngenite was confirmed by crystalloptical and thermographic investigations.

The crystalloptical constants of svngenite, natural and synthetic, were the following: synthetic syngenite $N_g$ 1.518, $N_p$ 1.501; natural syngenite (from Dzhaksy-Klych Lake) $N_g$ 1.519, $N_p$ 1.500.

The heating curve of a sample of the natural salt from the Dzhaksy-Klych Lake (Fig. 1) has thermal effects which are characteristic of syngenite and also of magnesium sulfate hydrates and astrakanite, contained in the sample.

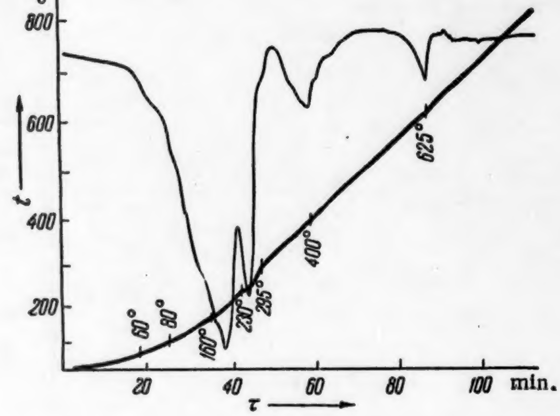


Fig. 2. Heating curve of carnallite.

The effect at 245° corresponded to syngenite dehydration, at 432° – its decomposition and at 590° – its conversion to potassium sulfate.

The thermal effects at 80, 155 and 360° corresponded to the dehydration of magnesium sulfate hexahydrate and kieserite and at 220° to astrakanite dehydration.

The syngenite was formed, most probably, by reactions of lake brine, containing up to 2% KCl, with gypsum, of which there are large deposits in the salt lake.

It should be noted that syngenite is rarely found in nature. It was first found in the Kalusha salt deposits (Stanislavskii region, Ukr. SSR) and named Kalushite [2].

Carnallite was the other potassium salt we found in the salt deposits taken from the surface of the Dzhaksy-Klych lake.

The carnallite crystallized from the brine as it evaporated in the summer. In addition to carnallite, crystals of magnesium sulfate hydrates and bischofite ($MgCl_2 \cdot 6H_2O$) were formed from the brine.

TABLE 2

| Salt | Content, weight % | Mineral | Content, weight % |
|---|---|---|---|
| $MgSO_4$ | 19.85 | Carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) | 58.52 |
| $MgCl_2$ | 21.11 | Hexahydrate ($MgSO_4 \cdot 6H_2O$) | 37.15 |
| KCl | 15.71 | Bischofite ($MgCl_2 \cdot 6H_2O$) | 2.24 |
| NaCl | 1.88 | NaCl | 1.88 |
| Σ . . . | 58.55 | Σ . . . | 99.79 |

Table 2 gives the chemical and mineralogical composition of salt samples taken from the surface of the Dzhaksy-Klych Lake (northern basin).

The heating curve of a sample of this salt is given in Fig. 2. The thermal effect on the curve at 60 and 80° corresponds to hexahydrate dehydration; at 160, 230 and 400° to carnallite dehydration and decomposition.

## LITERATURE CITED

[1] L. M. Grokhovskii, Coll. Work Mosgeolnerud (Moscow Geo.-Prospect. Trust of Nonmetal Min.), No. 1 (1950).*

[2] I. N. Lepeshkov, Potassium Salts of the Volga–Emba and Carpathian Regions, Acad. Sci. USSR Press, 1946.*

N. S. Kurnakov Institute of General and
Inorganic Chemistry
Academy of Sciences USSR

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* In Russian.

# DIENE CONDENSATIONS OF GEM-SUBSTITUTED BUTADIENES

Academician I. N. Nazarov and M. V. Mavrov

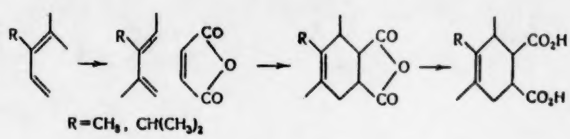
The question of whether or not gem-substituted butadienes undergo diene synthesis remained unsettled until recently. Except for a few papers [1-3], which appeared recently, the diene condensations of these dienes were only known from patent data.

At the same time, a series of authors reported that dienes of this type did not undergo this reaction at all [4], or, as shown for example in condensations with maleic anhydride, formed only polymeric products.

We undertook a detailed investigation of this kind of condensation. As the simplest gem-substituted dienes we took 1,1-dimethvl- (I), 1,1,2-trimethyl- (II), 1,1,3-trimethyl- (III), 1,1,4-trimethyl- (IV), 1,1-dimethyl--2-isopropyl- (V) butadienes and diisobutenyl (VI) and, with the exception of 1,1,3-trimethylbutadiene (III), we specially developed the preparation of these materials; as dienophils we used maleic anhydride, acrylonitrile, methyl acrylate and crotonaldehyde (see Table 1).

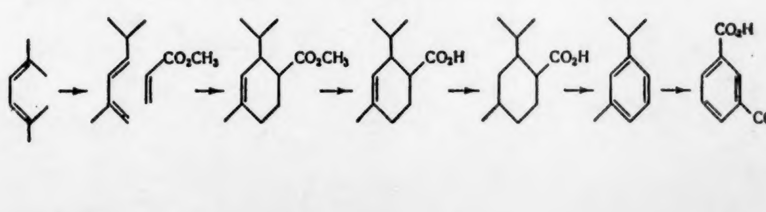
With maleic anhydride under various conditions (temperature, time, solvent, etc.) dienes I, IV and VI gave only polymeric products, while 1,1,2-trimethyl- (II) and 1,1-dimethyl-2-isopropyl- (V) butadienes with maleic anhydride (100°, 15hours) gave 40 and 70% yields, respectively, of adducts.

Further investigation showed that the compounds obtained corresponded to the adducts of isomeric forms of the starting dienes, i.e.,

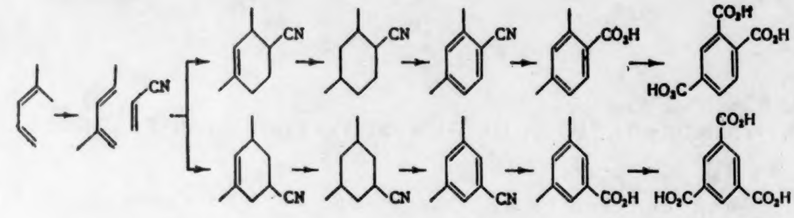



The use of dienophils of lower reactivities than maleic anhydride, required more drastic temperature conditions (for example, 230-260° for diisobutenyl), and the condensation of the dienes I, IV and VI was accompanied by considerable polymer formation and the total yields of condensation products were only 15-30%. Thus we were able to react all the dienes, which we studied (see Table 1). The structures of the adducts obtained were proved by dehydration of the materials over catalysts of chromium and aluminum oxides (with gem-dimethyl groups present, the dehydration over these was accompanied by only demethylation) or 20% palladium on charcoal, with subsequent oxidation to known aromatic acids.

From dehydration of the acid, obtained by hydrolysis of the adduct of diisobutenyl VI and methyl acrylate, both over $Cr_2O_3/Al_2O_3$ and over Pd/C and subsequent oxidation with dilute nitric acid under pressure, we isolated only isophthalic acid and not terephthalic acid, which would correspond to the normal addition product. The course of the reactions performed may be represented by the scheme:

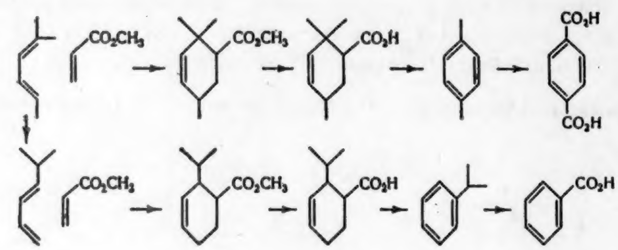


In the same way, the condensation of 1,1-dimethylbutadiene (I) proceeded with complete preliminary isomerization of the diene. In proving the structure we were able to demonstrate the presence of both structural isomers corresponding to 1,3-dimethylbutadiene, with approximately 5-7% of the meta isomer present.

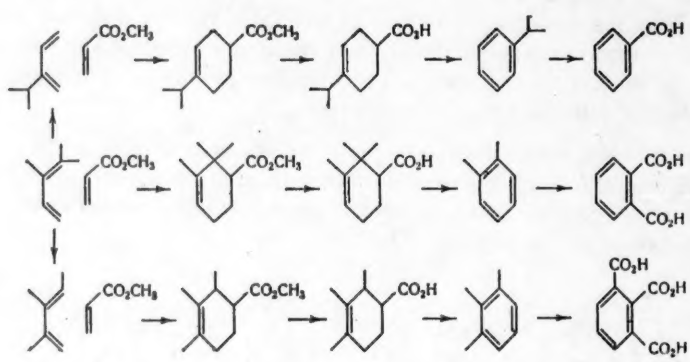



Apparently, during the reaction the original dienes undergo a rearrangement of the double bonds similar to the allyl rearrangement to form the 1,3-disubstituted butadienes. In a paper [5], which appeared during the course of this work, Alder and Schumacher reported the existence of this type of isomerization, but the authors completely denied the possibility of gem-substituted dienes' undergoing diene synthesis without preliminary isomerization. We were able to establish that some gem-substituted dienes can undergo diene condensation directly, but together with the adducts of normal structure, products are formed from isomeric forms of the original diene, which indicates partial isomerization of the dienes under the condensation conditions.

Thus, with methyl acrylate, 1,1,4-trimethylbutadiene (IV) forms a mixture of isomeric esters, containing about 60% of the normal adduct, and this was determined from the ratio of benzoic and terephthalic acids in the reaction products according to the scheme:

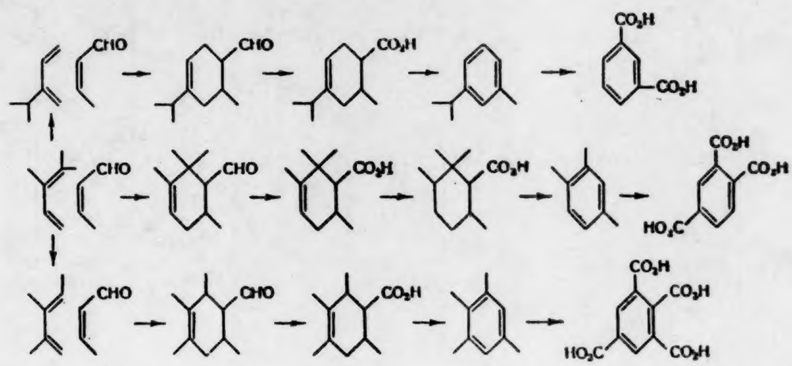



The condensation products of 1,1,2-trimethylbutadiene (II) and methyl acrylate was a mixture of at least three adducts, corresponding to the normal and the isomeric forms of diene II, whose presence was established by the following series of conversions:

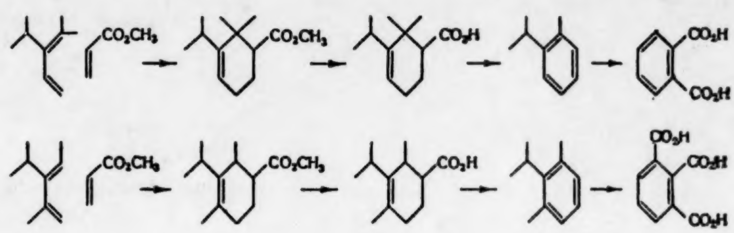


The benzoic, o-phthalic and hemimellitic acids thus isolated in a ratio of 1 : 2 : 5 approximately corresponded to the ratio of isomeric esters contained in the original mixture.

On oxidizing the mixture of aldehydes, obtained in the condensation of 1,1,2-trimethylbutadiene (II) with crotonaldehyde, with moist silver oxide we isolated crystalline 2,2,3,6-tetramethyl-$\Delta^3$-tetrahydrobenzoic acid (20-25% of the mixture of acids) in a pure form, whose structure was proved by conversion into trimellitic acid. Dehydrogenation of the residual mixture of acids and subsequent oxidation and separation gave isophthalic, trimellitic and prehnitic acids in approximately equal ratios. Thus the mixture of aldehydes contained about 50% of the adduct from normal addition.



We studied the behavior of 1,1-dimethyl-2-isopropylbutadiene (V) in condensation with methyl acrylate.



On dehydrating the mixture of acids, obtained by hydrolyzing the adduct, and oxidizing the product, we isolated o-phthalic and hemimellitic acids in the ratio of 1 : 3, i.e., in this case there was partial formation of the normal addition product.

The exception in this series of dienes is 1,1,3-trimethylbutadiene (III). As was known previously, the latter reacts with various dienophils very readily to give the normal adducts in good yields.

In the dehydration of the mixture of nitriles, obtained from the condensation of 1,1,3-trimethylbutadiene (III) with acrylonitrile, over $Cr_2O_3/Al_2O_3$ and subsequent hydrolysis and oxidation by the scheme:

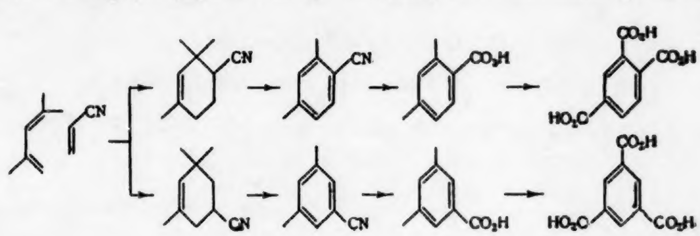


TABLE 1

| Dienes | Methyl acrylate | | | | | Acrylonitrile | | | | | Crotonaldehyde | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | experimental condition | | yield % | B. p. °C/mm Hg | $n_D^{20}$ | experimental condition | | yield % | B. p. °C/mm Hg | $n_D^{20}$ | experimental condition | | yield % | B. p. °C/mm Hg | $n_D^{20}$ |
| | °C | hours | | | | °C | hours | | | | °C | hours | | | |
|  | | | | | | 220 | 4 | 23 | 76—81/7 | 1.4708 | 150 | 14 | 18 | 85—90/16 | 1.4723 |
|  | 200 | 4 | 66 | 82—84/4 | 1.4701 | 200 | 5 | 72 | 98—101/7 | 1.4749 | 200 | 2 | 71 | 90—92/6 | 1.4778 |
|  | 220 | 2 | 67 | 69—72/3 | 1.4651 | 200 | 2 | 75 | 67—68/3 | 1.4705 | 200 | 2 | 18 | 87—89/15 | 1.4804 |
|  | 200 | 14 | 18 | 88—90/11 | 1.4535 | | | | | | 220 | 8 | 12 | 70—80/6 | 1.4720 |
|  | 170 | 7 | 64 | 94—97/4 | 1.4697 | 200 | 5 | 60 | 129—131/15 | 1.4787 | 200 | 4,5 | 40 | 83—86/3 | 1.4795 |
|  | 260 | 4 | 30 | 95—99/5 | 1.4662 | | | | | | 230 | 5 | 15 | 85—88/4 | 1.4758 |

together with trimellitic acid we isolated trimesic acid, corresponding to the metaisomer, which was present to the extent of 3-5%.

Thus it was established that 1,1-dimethylbutadiene and diisobutenyl only undergo diene synthesis after preliminary isomerization into 1,3-disubstituted dienes and do not form normal condensation adducts at all. 1,1,2-Trimethyl-, 1,1,4-trimethyl- and 1,1-dimethyl-2-isopropylbutadienes form the normal products of diene synthesis together with the adducts of isomeric forms of the geminal diene. Only 1,1,3-trimethylbutadiene undergoes diene synthesis normally.

## LITERATURE CITED


[1] G. Dupont, R. Dulou and G. Christen, Bull. Soc. Chim. 820 (1954).

[2] H. Euler and H. Hasselquist, Ark. Kemi, 6, 139 (1953).

[3] Y.-R. Naves and P. Ardizio, Helv. Chim. Acta 31, 2252 (1948).

[4] G. B. Bachmann and R. E. Hatton, J. Am. Chem. Soc. 66, 1512 (1944).

[5] Fortschritte der Chemie Organischer Naturstoffe, Wien, 10, 1953, S. 1-118.



N. D. Zelinskii Institute of Organic Chemistry
Academy of Sciences USSR



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# ALKYLATION OF PHENOL WITH DIISOBUTYLENE AND TRIISOBUTYLENE IN THE PRESENCE OF CATALYSTS CONTAINING BORON TRIFLUORIDE

Academician A. V. Topchiev, B. M. Tumerman and T. A. Fedorova

As was reported earlier [1], phenols are alkylated in high yield by the lower olefins, isobutylene and isoamylene in the presence of catalysts containing boron trifluoride. This led us to expect that such catalysts as the ethyl etherate of boron trifluoride $(C_2H_5)_2O \cdot BF_3$, orthophosphoric acid saturated with boron trifluoride $H_3PO_4 \cdot BF_3$ and boron trifluoride monohydrate $H_2O \cdot BF_3$ would also be active catalysts in the alkylation of phenol with diisobutylene $C_8H_{16}$ and triisobutylene $C_{12}H_{24}$.

The alkylating hydrocarbons, diisobutylene and triisobutylene were prepared by polymerization of isobutylene in the presence of boron trifluoride ethyl etherate. The method of preparing diisobutylene and triisobutylene and their structures have been published [2, 3]. Basic constants: for diisobutylene b. p. 100-110°, $n_D^{20}$ 1.4105, $d_{20}^{20}$ 0.7216, aniline point 40; for triisobutylene b. p. 175-180°, aniline point 73.5, $n_D^{20}$ 1.4329, $d_{20}^{20}$ 0.7216.

The catalysts—boron trifluoride ethyl etherate, orthophosphoric acid saturated with boron trifluoride and boron trifluoride monohydrate—were prepared by passing gaseous boron trifluoride into diethyl ether, orthophosphoric acid and water. In the reaction of gaseous boron trifluoride with diethyl ether, orthophosphoric acid and water, molecular compounds of these substances were formed. Their preparation, physicochemical characteristics and catalytic properties have been described [4].

In a series of experiments we studied the yield of alkylate (p-tert.-octylphenol and dodecylphenol) in relation to the nature of the catalyst, its optimal amount, the reaction temperature, the reaction time and the ratio of the reaction components.

The experiments were performed in the following way. Into a round-bottomed, three-necked flask, fitted with a mechanical stirrer, a reflux condenser and a dropping funnel, was placed 50 g (0.5 mole) of freshly distilled molten phenol. Various amounts of the catalysts studied (see Table 1) were added to the phenol. After this the stirrer was started and 30 g of diisobutylene (0.5 mole per mole of phenol) or triisobutylene (in a ratio varying from 0.5 to 1 mole per mole of phenol) was added dropwise. The temperature of the mixture was kept constant with continuous stirring.

At the end of the reaction, the reaction mixture was washed with hot water in a separating funnel until neutral to congo, dried over calcium chloride and vacuum distilled (10 mm pressure).

Alkylation of phenol with diisobutylene and triisobutylene in the presence of boron trifluoride ethyl etherate $(C_2H_5)_2 \cdot O \cdot BF_3$. The reaction was performed by the method described above. The amount of catalyst, reaction temperature and reaction time were varied in this series of experiments on the alkylation of phenol with diisobutylene (Table 1).

In the alkylation of phenol with triisobutylene we studied the alkylate yield in relation to the amount of catalyst, the temperature, the reaction time and the ratio of olefin to phenol (see Figs. 1-3).

Table 1 shows that the alkylate yield increases when the amount of catalyst is increased from 1 to 5% on phenol. Increasing the amount of catalyst to 10% does not raise the alkylate yield. Raising the reaction temperature and the reaction time decreases the alkylate yield.

Figure 2 shows that the alkylate yield increases when the amount of catalyst is increased from 1 to 5%. The optimal conditions for alkylating phenol with triisobutylene are the following: reaction time, 3 hours; temperature, 70°; amount of catalyst, 5% on phenol.

TABLE 1

Effect of Amount of Catalyst $(C_2H_5)_2O \cdot BF_3$ and Reaction Temperature and Time on the Alkylation of Phenol with Diisobutylene

| Taken for reaction | | | | Reaction conditions | | Products obtained, % | | | |
|---|---|---|---|---|---|---|---|---|---|
| phenol g | diisobutylene, g | catalyst g | catalyst % | temp., °C | time, hours | phenol | alkylate | residue | losses |
| 50 | 30 | 2.5 | 10 | 50 | 2 | 16.2 | 76.0 | 5.9 | 1.9 |
| 50 | 30 | 1.25 | 5 | 50 | 2 | 15 | 76.5 | 6.0 | 2.5 |
| 50 | 30 | 0.25 | 1 | 50 | 2 | 19 | 73.6 | 4.9 | 2.5 |
| 50 | 30 | 0.25 | 1 | 70 | 2 | 37 | 54.6 | 5.1 | 3.9 |
| 50 | 50 | 0.25 | 1 | 70 | 3 | 53 | 40.6 | 30 | 4.0 |

Alkylation of phenol with diisobutylene and triisobutylene in the presence of orthophosphoric acid saturated with boron trifluoride $H_3PO_4 \cdot BF_3$ and boron trifluoride monohydrate $H_2O \cdot BF_3$. The experimental procedures were not changed. The results of this series of experiments on the alkylation of phenol with diisobutylene are given in Table 2 and with triisobutylene, in Figs. 1 and 3.

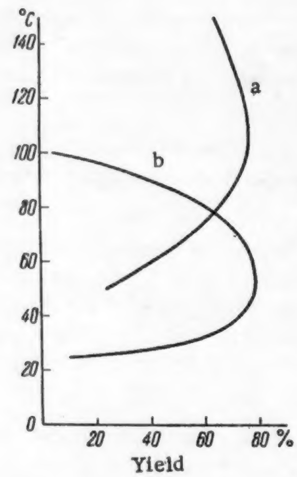


Fig. 1. Alkylate yield in relation to temperature. Catalysts; a) $H_3PO_4 \cdot BF_3$ (10%); b) $H_2O \cdot BF_3$ (10%).

Table 2 shows that increasing the reaction temperature from 50 to 100°, the amount of catalyst from 1 to 5% and the reaction time from 2 to 4 hours increased the alkylate yield by 5%.

The alkylation of phenol with diisobutylene in the presence of boron trifluoride monohydrate was performed under the optimal conditions for $H_3PO_4 \cdot BF_3$. We used 50 g of phenol and 30 g of diisobutylene, the reaction temperature was 50° and the reaction time 2 hours; under these conditions the alkylate yield equalled 38% of the theoretical. The results of alkylating phenol with triisobutylene are illustrated in Figs. 1 and 3, which show that the alkylate yield (catalyst $H_3PO_4 \cdot BF_3$) is raised on increasing the amount of catalyst from 5 to 10% and on increasing the reaction time from 1 to 4 hours. With the catalyst, $H_2O \cdot BF_3$, the alkylate yield increases on raising the temperature from 25 to 50° but at 100° it decreases considerably.

Investigation of alkylation products. The p-tert.-octylphenol obtained was washed with hot water until neutral to congo, dried and vacuum distilled at 10 mm pressure. We obtained oily and crystalline products.

The crystalline products were recrystallized several times from ethyl alcohol or isooctane. Recrystallization from acetic acid or normal heptane gave poor results. After recrystallization from isooctane, the octylphenol melted at 68-70° (melting point of pure octylphenol, 73-74°).

The oily products were the corresponding phenol ethers and were not examined in detail.

Properties of p-tert.-octylphenol: b. p. 100-154°, M = 210, m. p. 68-70°, OH (by Tserevitinov [Zerewitinoff] method) 5%.

TABLE 2

Effect of Amount of Catalyst $H_3PO_4 \cdot BF_3$ and Reaction Temperature and Time on the Alkylation of Phenol with Diisobutylene

| Taken for reaction | | | Reaction conditions | | Products obtained, % | | | |
|---|---|---|---|---|---|---|---|---|
| phenol, g | diisobutylene, g | catalyst % | temp., °C | time, hours | phenol | alkylate | residue | losses |
| 50 | 30 | 5 | 100 | 4 | 38.2 | 54.5 | 50 | 2.3 |
| 50 | 30 | 1 | 100 | 4 | 38 | 54.9 | 4.8 | 2.1 |
| 50 | 30 | 1 | 50 | 2 | 45.0 | 48.0 | 4.0 | 3.0 |
| 50 | 30 | 2 | 50 | 2 | 45.1 | 47.9 | 41 | 2.9 |

The dodecylphenol obtained was washed with hot water until neutral to congo and vacuum distilled (5 mm pressure). We collected fractions at 100-150° (crystals) and 150-165° (oily). The crystalline fraction was recrystallized from ethyl alcohol. The dodecylphenol melted at 62-64°.

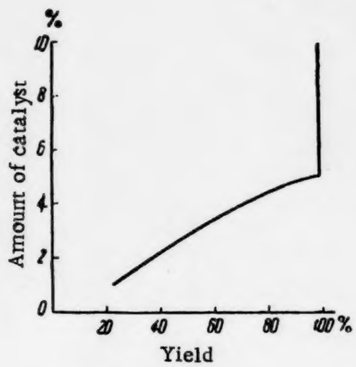


Fig. 2. Alkylate yield in relation to amount of catalyst $(C_2H_5)_2O \cdot BF_3$ (70°, 3 hours).

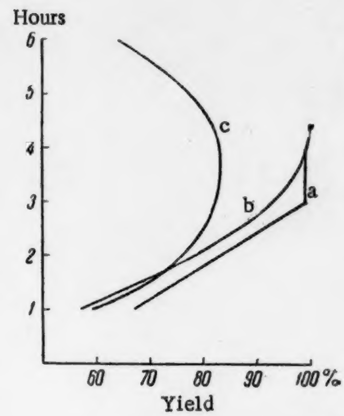


Fig. 3. Alkylate yield in relation to reaction time. Catalysts. a) $(C_2H_5)_2 \cdot BF_3$ (10%, 70°), b) $H_2O \cdot BF_3$ (20%, 50°), c) $H_3PO_4 \cdot BF_3$ (10%, 100°).

Properties of dodecylphenol fractions: fraction I, b. p. 100-155°/5 mm, M = 258, m. p. 62-64°, OH (by Tserevitinov method) 6.1%, fraction II, 155-165°/5 mm, M = 262°.

## LITERATURE CITED

[1] A. V. Topchiev, B. M. Tumerman, V. N. Andronov and L. N. Korshunova, Petr. Ind. No. 7 (1954).*

[2] A. V. Topchiev, B. M. Tumerman and V. N. Andronov, Proc. Acad. Sci USSR 74, No. 1 (1950).

[3] A. V. Topchiev, B. M. Tumerman and V. N. Andronov, Proc. Acad. Sci. USSR 74, No. 3 (1950).

[4] A. V. Topchiev, Ia. M. Paushkin and O. V. Zavgorodnii, Prog. Chem. 21, No. 4 (1952).*

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* In Russian.

## PREPARATION OF ISOPRENE BY CATALYTIC DEHYDROGENATION OF ISOPENTENES

Academician A. A. Balandin, O. K. Bogdanova and A. P. Shcheglova

The solution of the problem of isoprene polymerization and the preparation of isoprene caoutchouc, with properties surpassing those of natural caoutchouc, have created the problem of developing a method for synthesizing isoprene. The cheapest and most advantageous raw material for preparing isoprene is petroleum and its reprocessing products. The petroleum industry has large stocks of isopentane and isopentenes which could be used for preparing isoprene by catalytic dehydrogenation.

According to the literature data [1-4], isopentenes diluted with water vapor in a ratio of 1 : 7.5-18.8 volumes are dehydrogenated at 635-650° and a flow rate of 319-476 volumes per volume of catalyst per hour. The isoprene yields, under these conditions, are 35% of the isopentenes passed and 65-74.5% of the isopentenes decomposed. The reaction proceeds for an hour and then the catalyst is regenerated for an hour.

We investigated the catalytic dehydrogenation of isopentenes. In order to find the optimal conditions for the reaction, the experiments were carried out at various temperatures and rates of isopentene introduction and with water vapor dilution. As a solvent water vapor has advantages as besides lowering the partial pressure of the hydrocarbon, it can also act as a heat carrier, it is readily separated from the reaction products, and, moreover, it removes the carbonaceous deposits from the catalyst and thus considerably increases the operating time of the catalyst without need of regeneration.

The amylenes for the experiments (mixture of isomers, with b. p. 21-37°) were prepared by dehydrating isoamyl alcohol over aluminum oxide and were purified by distillation on a column of 60 t.p. The experiments were carried out in a flow system. The apparatus was the same as in [5]. The initial hydrocarbons were introduced from a tank. The input rate was regulated with a needle valve and controlled by a rheometer. Before entering the furnace, the isopentene vapor was saturated with water vapor to the required ratio in a saturator. The reaction products passed from the furnace into a receiver with a reflux condenser, where the water vapor was condensed and collected in a trap, placed in a Dewar flask cooled with a mixture of $CO_2$ and acetone. The gas evolved was collected in a gasometer over a saturated solution of NaCl. The gas volumes were corrected to n.t.p. The gas collected was analyzed on a modification of the Orsat-Eger apparatus. The isoprene content of the catalyzate was determined with maleic anhydride. The total unsaturated and saturated hydrocarbons were determined in the gas phase, obtained by evaporating a catalyzate sample in a current of nitrogen into a cylindrical gasometer over a saturated solution of NaCl. The hydrocarbon content of the gas was maintained at not higher than 15-16% in order to avoid condensation.

We investigated the effect of temperature, input rate and degree of dilution with water vapor on the isoprene yield. The results of experiments on the effect of temperature (540-635°) on the dehydrogenation at various flow rates are given in Table 1. By raising the temperature from 540 to 600°, at a flow rate of ~5000 ml/liter · hour, the isoprene yields increased from 18.4 to 30.6%. At the same flow rate the isoprene yields were 29% at 620° and 26.4% at 635°. Figure 1 shows the relation of isoprene yield to temperature.

The effect of the input rate on the process was investigated in the same temperature range by varying the input rate of isopentenes from 3500 to 8100 ml/liter · hour. Table 1 shows that at 540-560° the isoprene yield maximum was displaced towards lower rates. At a temperature of 580-600°, the change in flow rate from 4300 to 7800 ml/liter · hour hardly affected the isoprene yields; at 600° the isoprene yields changed from

29.7 to 31.4% of the isopentenes passed and from 88 to 92% of isopentenes reacted (Fig. 2). With a rise in temperature the yield maximum was displaced towards greater input rates as the thermal conversion of isoprene was considerably accelerated by higher temperatures. At an input rate of 8100 ml/liter·hour and at 620°, the isoprene yield reached 36.4% of the isopentene passed.

TABLE 1

Dehydrogenation of Isopentenes at Various Temperatures and Flow Rates

| Expt. No. | Temperature, °C | Input rate of isopentenes, ml/liter·hr. | Dilution with water vapor $C_5H_{10}$ wt. : $H_2O$ | Isoprene yield,* wt. % of isopentene passed | Gas analysis, vol. % | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $CO_2$ | $C_4$ | $C_2H_4$ | $H_2$ | $CH_4$ | $C_2H_6$ |
| 57 | 540 | 5000 | 1:2.7 | 18.4 | 1.8 | 0.8 | — | 95.2 | 2.2 | — |
| 96 | | 6050 | 1:2.2 | 14.3 | 2.2 | 0.8 | — | 94.4 | 2,6 | — |
| 88 | | 6500 | 1:2.9 | 12.3 | 1.0 | 0.8 | — | 95.4 | 2.7 | — |
| 63 | 560 | 3500 | 1:3.0 | 21.2 | 2.8 | 0.4 | 0.4 | 93.8 | 2.6 | — |
| 66 | | 4400 | 1:2.9 | 22.9 | 2.6 | 0,6 | 0.4 | 94.0 | 2.4 | — |
| 93 | | 6500 | 1:2.5 | 19.4 | 2.6 | 0.6 | 0.4 | 94.2 | 2.2 | — |
| 84 | | 8500 | 1:3.0 | 14.9 | 2.2 | 0.6 | 0.2 | 94.6 | 2.3 | — |
| 61 | 580 | 3900 | 1:2.9 | 25.7 | 4.8 | 0.5 | 0.8 | 89.6 | 4.4 | — |
| 65 | | 4700 | 1:2.4 | 26.4 | 4.6 | 0.4 | 0.4 | 90.2 | 4.3 | — |
| 47 | | 5600 | 1:2.9 | 27.4 | 3.8 | 0.8 | 0.2 | 92.0 | 3.2 | — |
| 85 | | 7200 | 1:3.2 | 24.5 | 3.0 | 1.2 | 0.2 | 92.0 | 3.5 | — |
| 92 | | 8100 | 1:2.2 | 25.6 | 2.4 | 1.0 | 0.2 | 94.0 | 2.3 | — |
| 58 | 600 | 4920 | 1:2.6 | 30.6 | 6.3 | 2.6 | 1.6 | 86.4 | 2,1 | 1.0 |
| 43 | | 6700 | 1:3.0 | 31.5 | 4.0 | 0.8 | 0.2 | 91.4 | 3.7 | — |
| 91 | | 7300 | 1:2.4 | 31.4 | 3.4 | 0.8 | 0.2 | 92.0 | 3.6 | — |
| 83 | | 7800 | 1:3.0 | 30.0 | 3.0 | 0.8 | 0.1 | 93.0 | 3.1 | — |
| 55 | 620 | 5560 | 1:2.5 | 29.1 | 6.4 | 1.2 | 1.2 | 81.6 | 6.1 | 2.4 |
| 81 | | 6660 | 1:3.2 | 32.8 | 6,4 | 1.4 | 0.6 | 85,6 | 5.8 | — |
| 103 | | 7900 | 1:2.5 | 35.8 | 5.6 | 0.6 | 0.6 | 87.6 | 5.4 | — |
| 95 | | 8100 | 1:2.2 | 36.4 | 6.0 | 1.0 | 0.6 | 86.8 | 5.6 | — |
| 53 | 635 | 5800 | 1:2.4 | 26.4 | 8.2 | 2.3 | 2.3 | 72.2 | 12.1 | 2.8 |
| 156 | | 6370 | 1:2.9 | 25.5 | 7.6 | 2,7 | 2.1 | 73.2 | 12.0 | 2.4 |
| 112 | | 8000 | 1:2.3 | 26.2 | 6.4 | 1.2 | 1.2 | 79.2 | 10.0 | 2.0 |

*Isoprene yields calculated on reacted isopentenes in relation to the flow rate: at 540° 95-97 weight %; at 560° 93-96 weight %; at 580° 90-94 weight %; at 600° 88-93 weight %; at 620° 84-90 weight %; at 635° 74-84 weight %.

In order to elucidate the effect of the degree of dilution with water vapor on the process, we carried out two series of experiments at 560 and 580° and an input rate of 6500 ml/liter·hour. The dilution of isopentenes with water vapor was varied from 1:1.2 to 1:4.2 (by weight). As can be seen from Fig. 3, the maximum on the curves corresponds to an isopentene dilution with water vapor in a ratio of 1:2.3-3.3 (by weight). With a decrease in the degree of dilution, the formation of light hydrocarbons and $CO_2$ increased and the isoprene yield decreased. In experiments carried out without dilution, the isoprene yields were only 8.6% at 580° and 7.4% at 560°.

Thus, the best conditions for dehydrogenating isopentenes into isoprene are: a temperature of 580-620° an input rate of 5000-8000 ml per liter of catalyst per hour and dilution with water vapor in a ratio of 1:2.3-3.3 (by weight). The process may be continued for a long time without catalyst regeneration.

We also carried out balance experiments at 600°, an isopentene input rate of 6700-7200 ml/liter·hour and dilution with water vapor in a ratio of 1:3 (by weight). The experiments lasted 2-3 hours. The results are given in Table 2. The catalytic gas consisted of hydrogen (89-90%) with a small amount of $CO_2$, $C_2H_4$ (0.4%), $C_4$ hydrocarbons (1.6%) and $CH_4$ (4.2%). The degree of decomposition of the isopentenes was 30-31.5%. Besides the main reaction of isopentene dehydrogenation into isoprene in a 28.8-28.2% yield on the isopentene passed and 91.3-91.7% on isopentene decomposed, there also occurred demethanation to give butylene and butadiene (total 1.6%), hydrogenation of isopentene to isopentane (0.4%) and isoprene decomposition to give

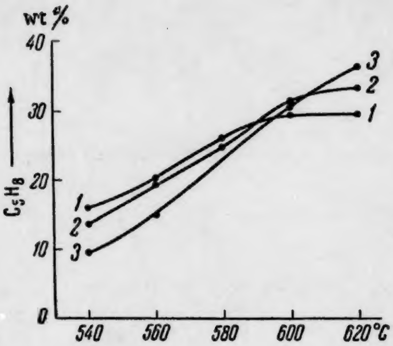


Fig. 1. The effect of temperature on isoprene yield at various flow rates: 5600 ml/liter·hour, 2) 6700 ml/liter·hour, 3) 7900 ml/liter·hour.

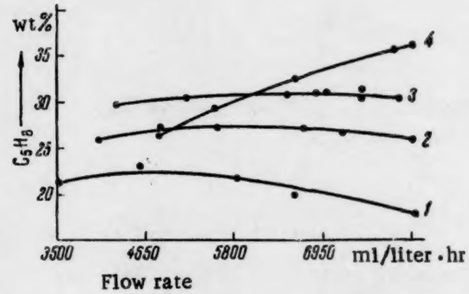


Fig. 2. The effect of flow rate on the isoprene yields at various temperatures: 1) 560°, 2) 580°, 3) 600°, 4) 620°.

TABLE 2

Isopentene Dehydrogenation at 600°, 7000 ml/liter·hour Input Rate and Dilution with Water Vapor in a Ratio of 1 : 3 (by weight)

| $C_5H_{10}$ passed, g | Catalyzate collected, g | Composition of reaction products, weights % of isopentene passed | | | | | | | | Degree of conversion of $C_5H_{10}$, % | Isoprene yield on reacted $C_5H_{10}$ wt. % | Gas collected liters (n.t.p.) | Gas analysis, vol. % | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $CO_2$ | $CH_4$ | $C_2H_4$ | $C_4H_8$ | $C_4H_6$ | $C_5H_8$ | $C_5H_{10}$ | $C_5H_{12}$ | | | | $CO_2$ | $C_2H_4$ | $C_4$ | $H_2$ | $CH_4$ |
| 46.3 | 45.8 | 0.29 | 0.3 | 0.1 | 1.4 | 0.2 | 28.2 | 69.2 | 0.5 | 30.7 | 91.3 | 4.9 | 4.4 | 0.4 | 1.6 | 89.4 | 4.2 |
| 44.4 | 44.0 | 0.23 | 0.3 | 0.1 | 1.6 | 0.2 | 28.8 | 68.6 | 0.2 | 31.4 | 91.7 | 4.8 | 3.4 | 0.4 | 1.0 | 90.6 | 4.6 |

light gases and carbon dioxide (0.3%). The carbon dioxide formed as a result of the carbonaceous deposits on the catalyst reacting with water vapor by the reaction: $C + 2H_2O = 2H_2 + CO_2$.

We also studied the kinetics of isopentene dehydrogenation into isoprene. The experiments were carried out in the temperature range 530-590°, at a flow rate of 7000 ml/liter·hour and dilution with water vapor in a ratio of 1 : 3 (by weight). We found that at 560° the adsorption coefficients of isopentene and the reaction products, hydrogen and isoprene, calculated by the formula (5):

$$z = \frac{\frac{m_0}{m} - 1}{\frac{100}{p} - 1},$$

were in the ratio 1 : 0.8 : 3.55, i.e., isoprene was adsorbed more strongly on catalytically active surface than isopentene, and hydrogen was adsorbed almost the same as isopentene; with an increase in temperature the relative adsorption coefficient of hydrogen

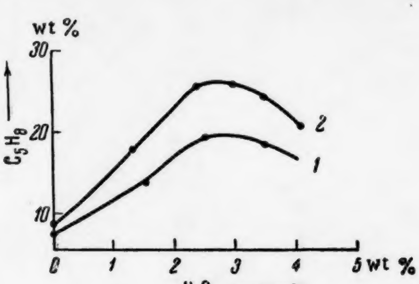


Fig. 3. The effect of the degree of dilution with water vapor on the isoprene yield at a temperature of: 1) 560°, 2) 580°.

remained unchanged, but that of isoprene decreased to 2.8 at 580°. The rate constant of the reaction, calculated by the formula (5):

$$\frac{dx}{dt} = K \frac{[A_1]}{[A_1] + z_2[A_2] + z_3[A_3]},$$

changes from 4.3 ml/min at 530° to 12.25 ml/min at 590°. The activation energy of the dehydrogenation was 23.3 kcal/mole.

## LITERATURE CITED


[1] A. Grosse, Ch. E. Morrell and J. M. Mavity, Ind. and Eng. Chem. 32, 309 (1940).

[2] J. M. Mavity and E. E. Zetterholm, Trans. Am. Inst. Chem. Engs. 40, 473 (1944).

[3] USA Pat. 2440471 (1948); Chem. Abstr. 42, 5464 (1948).

[4] USA Pat. 2442319 (1948); Chem. Abstr. 42, 6106 (1948).

[5] A. A. Balandin, O. K. Bogdanova and A. P. Shcheglova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1946, 497; 1955, 723.*



N. D. Zelinskii Institute of Organic Chemistry
Academy of Sciences USSR



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# REACTION OF DIACETYLENE WITH ETHYL MERCAPTAN AND SOME PROPERTIES OF THE COMPOUNDS OBTAINED

A. V. Bogdanova, M. F. Shostakovskii and G. I. Plotnikova

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Syntheses with diacetylene have made it possible to prepare a series of ethynylvinyl ethers [1, 3], which are interesting from the point of view of their reactivity and the preparation of 1-alkoxybutadienes-1,3 from them [4]. In these papers it was shown that alcohols of the aliphatic and hydroaromatic series react smoothly with diacetylene to form the corresponding ethynylvinyl ethers and acetals of the butynyl type $CH\equiv C-CH=CH-OR$ and $CH_3-C\equiv C-CH(OR)_2$. It seemed interesting to study the reaction of diacetylene with mercaptans also. On this subject the literature contains only a patent [5] describing the reaction of diacetylene and butyl mercaptan and benzyl mercaptan. The only products isolated by the authors were the corresponding ethynylvinyl ethers. The example of a reaction of diacetylene with a mercaptan that we studied involved ethyl mercaptan, which is readily available and its reaction with diacetylene has not been described. We found that ethyl mercaptan even reacted with diacetylene with slight heating of the mxiture and that in the presence of alkali the reaction began at room temperature and was accompanied by self-heating. The presence of azoisobutyronitrile hardly produced any additional initiation of the reaction, indicating that the first stage of the reaction of diacetylene with mercaptans proceeds mainly by an ionic mechanism. The reactions follow scheme (I) and, depending on the ratio of the starting materials and the temperature, give rise to ethynylvinyl thioethyl ethers and the product of the addition of two molecules of mercaptan (II), which has a butadiene structure.

$$CH\equiv C-C\equiv CH \xrightarrow{RSH} \overset{\mathrm{I}}{CH\equiv C-CH=CH-SR} \xrightarrow{RSH}$$

$$\rightarrow \overset{\mathrm{II}}{RS-CH=CH-CH=CH-SR} \qquad (1)$$

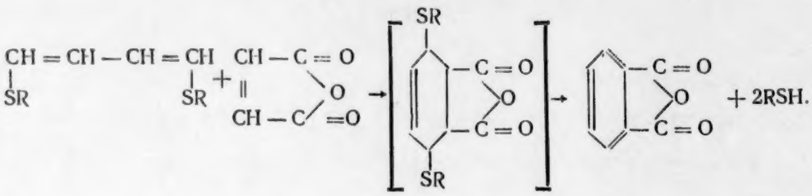
The reaction proceeds stepwise as is proved by the possibility of the second stage proceeding indeppendently and with another mercaptan. However, the addition of a mercaptan to the ethynylvinyl thioethyl ether may proceed under the influence of various reagents and factors: alkali, HCl, radical initiators and heating. In the two latter cases, the reaction gives high yields of end products which indicate that the addition of a mercaptan to an ethynylvinyl thioethyl ether proceeds more readily by a radical mechanism than by an ionic one. In this case the main reaction products are dithioalkylbutadienes-1,3:

$$CH\equiv C-CH=CH-SR+R'SH\rightarrow R'S-CH=CH-CH=CH-SR$$

$$\text{or } CH_2=C(SR')-CH=CH-SR$$

$$R \text{ and } R'=C_2H_5 \text{ (III)};\ R=C_2H_5\ R'=C_6H_5 \text{ (IV)} \qquad (2)$$

This is supported by the fact that the products obtained by ionic and radical mechanisms react with maleic anhydride to give adducts from diene synthesis with the elimination of two molecules of mercaptan during the reaction to form phthalic anhydride:



(3)

Some difference in the physical constants and a high exalation of molecular refraction for the product from the addition of two molecules of mercaptan to diacetylene is apparently explained by the presence of isomeric compounds, which may include other isomeric products besides the compounds with a butadiene structure. To prove the structures of the compounds isolated, we used the method of mercuric chloride titration, which one of us and Prilezhaeva [6, 7] proposed for the determination of vinyl thioalkyl ethers. The ethynylvinyl thioethyl ether reacted with an alcohol solution of mercuric chloride with quantitative formation of ethyl mercaptomercury chloride, an equivalent amount of HCl and, apparently, ethynylvinyl ethyl ether by equation (4)

$$\begin{array}{l} CH \equiv C - CH = CH - S - C_2H_5 + HgCl_2 + C_2H_5OH \rightarrow \\ \rightarrow C_2H_5SHgCl + HCl + [CH \equiv C - CH = CH - OC_2H_5] \end{array} \qquad (4)$$

and, consequently, this method may be used for the quantitative determination of ethynylvinyl thioalkyl ethers. The action of an aqueous solution of mercuric chloride on ethynylvinyl thioethyl ether and the product with two mercapto groups leads to incomplete decomposition of the starting materials. In this case the ethyl mercaptomercury chloride and HCl liberated represent on an average 40 and 60%, respectively.

$$\begin{array}{l} CH \equiv C - CH = CH - SC_2H_5 + H_2O + HgCl_2 \rightarrow \\ \rightarrow C_2H_5SHgCl + HCl + (CH_3 - C \equiv C - CHO). \end{array} \qquad (5)$$

Reaction of diacetylene with ethyl mercaptan. Into a reaction apparatus, fitted with a stirrer and a reflux condenser, connected to a spiral trap, was placed a 2% solution of potassium hydroxide in 26.1 g of ethyl mercaptan (b. p. 36-36.5°) and 20 ml of dioxane. Seven g of diacetylene was absorbed at 65-70° and then the mixture was stirred at the same temperature for 1 hour more. At the end of the reaction the mixture was washed several times with water, dried over potassium carbonate and vacuum distilled:

Fraction I 47-50°/8 mm 9.1 g;

Fraction II 112-120°/5 mm 4.6 g;

Residue 1.9 g.

Fraction I was ethynylvinyl thioethyl ether with b. p. 65-65.6°/17 mm; $n_D^{20} = 1.5468$; $d_4^{20} = 0.9516$. Found $MR_D = 37.38$; calculated for $C_6H_8S$ |=|≡ $MR_D = 35.35$. The yield was 58.1% of theoretical.

Found %: C 64.02, 64.32; H 7.29, 7.18; S 27.96. $C_6H_8S$. Calculated %: C 64.23; H 7.19; S 28.58.

After two distillations fraction II had the following constants: b. p. 116.0°/5 mm; $n_D^{20} = 1.5853$; $d_4^{20} = 1.0193$. Found $MR_D = 57.34$; calculated for $C_8H_{14}S_2$ 2|= $MR_D = 54.15$ and was the product from the addition of two molecules of mercaptan to diacetylene (II). The yield was 18.8% of theoretical.

Found %: C 54.86, 54.86; H 7.78, 7.94. $C_8H_{14}S_2$. Calculated %: C 55.12; H 8.09.

The product did not show a reaction for an acetylene bond with an ammonia solution of $AgNO_3$ and on adding excess of mercuric chloride solution, the two products isolated showed an acid reaction to methyl orange. The experiments performed under different conditions are reported in Table 1.

Decomposition of ethynylvinyl thioethyl ether (I) and the product with two mercapto groups (II) with an alcohol solution of mercuric chloride. Into a conical flask was placed a sample of the material and 6-7 ml of a 20% solution of mercuric chloride in ethyl alcohol (containing 2.2 times the amount of mercuric chloride theoretically required according to reaction (4)). A light precipitate precipitated immediately and this settled to the bottom when the solution stood for a day. The contents of the flask were diluted with 25 ml of distilled water and titrated with 0.1 N NaOH in the presence of methyl orange. After the titration, the precipitate of ethyl mercaptomercury chloride was filtered off into a weighed glass filter, washed with hot xylene and dried in a vacuum desiccator. The ethyl mercaptomercury chloride isolated did not melt on heating to 200° and decomposed at about 320° (5). The results of titration and the yield of ethyl mercaptomercury chloride are given in Table 2.

TABLE 1

Reaction of Diacetylene with Ethyl Mercaptan

| Expt. No. | Reagent | Molar ratio, diacetylene: mercaptan | Time in hours | T., °C | Yield of ether in % of theoretical | Yield of butadiene in % of theoretical |
|---|---|---|---|---|---|---|
| 1 | KOH | 1 : 1 | 1 | 18—60 | 48.2 | Traces |
| 2 | KOH | 1 : 2 | 1 | 50—55 | 46.7 | 5.4 |
| 3 | KOH | 1 : 3 | 1 | 50—55 | 68.0 | 6.8 |
| 4 | KOH | 1 : 3 | 1 | 65—70 | 58.1 | 18.8 |
| 5 | KOH | 1 : 3 | 2 | 65—70 | 50.0 | 33.0 |
| 6 | — | 1 : 1 | 2 | 50—55 | ~10.0 | — |
| 7 | Nitrile | 1 : 1 | 2 | 50—55 | ~10.0 | — |

Hydrolysis of ethynylvinyl thioethyl ether and the product with two mercapto groups in the presence of mercuric chloride. A sample of the material was mixed with excess of a 5.5% solution of mercuric chloride in water. We immediately observed the formation of a light precipitate of ethyl mercaptomercury chloride and a tarry mass, which settled on the walls of the flask. After standing for some time, the solution was titrated with 0.1 N NaOH and then the precipitate was filtered off, carefully washed with acetone to remove tar, dried and weighed. The ethyl mercaptomercury chloride isolated did not melt on heating at 230°. The results of the experiments are given in Table 3.

TABLE 2

Quantitative Determination of Ethynylvinyl Thioethyl Ether

| Expt. No. | Sample of ether in g | 0.1 N NaOH consumed in ml | Thioether found as % of theoretical | Yield of ethyl mercaptomercury chloride in g | Yield of ethyl mercaptomercury chloride in % of theoretical |
|---|---|---|---|---|---|
| 1 | 0.2042 | 18.20 | 99.91 | 0.52 | 96.1 |
| 2 | 0.2076 | 18.56 | 100.2 | 0.53 | 96.5 |

Reaction of ethynylvinyl thioethyl ether with ethyl mercaptan and thiophenol. The reaction was performed in sealed ampules or in a flask, at various temperatures and in the presence of various reagents (Table 4).

The product with two mercapto groups (II), obtained in the presence of azoisobutyronitrile had the following constants: b. p. 120.0°/5 mm; $n_D^{20} = 1.6062$, $d_4^{20} = 1.0134$; $MR_D = 59.29$. Calculated for $C_8H_{14}S_2 2F$ = 54.15.

Found %: C 55.26, 55.12; H 8.28, 8.16; S 36.59, 36.65. $C_8H_{14}S_2$. Calculated %: C 55.12; H 8.09; S 36.78.

TABLE 3

Hydrolysis of Ethynylvinyl Thioethyl Ether and Dithioethylbutadiene-1,3 in the Presence of Mercuric Chloride

| Expt. No. | Sample in g | 0.1 N NaOH consumed in ml | Found, as % of theoretical | | Yield of ethyl mercapto-mercury chloride | |
|---|---|---|---|---|---|---|
| | | | ether | buta-diene | in g | in % of theoretical |
| 1 | 0.2114 | 7.81 | 41.4 | — | 0.26 | 46.4 |
| 2 | 0.1942 | 7.31 | 42.2 | — | 0.25 | 48.1 |
| 3 | 0.1832 | 6.90 | — | 32.38 | 0.40 | 64.0 |
| 4 | 0.1856 | 7.01 | — | 32.46 | 0.41 | 64.8 |

Constants of dithio(ethylphenyl)butadiene-1,3 (III) isolated. B. p. 165.0-165.2°/2.5 mm; $n_D^{20}$ = 1.6697; $d_4^{20}$= 1.0990; $MR_D$ = 76.56. Calculated for $C_{12}H_{14}S_25$ $MR_D$ = 69.02.

Found %: C 64.79, 64.64; H 6.36, 6.32; S 29.20, 29.30. $C_{12}H_{14}S_2$. Calculated %: C 64.81; H 6.34; S 29.51.

TABLE 4

Reaction of Ethynylvinyl Thioethyl Ether with Ethyl Mercaptan and Thiophenol

| Expt. No. | Reagent | Reaction temperature in °C | Reaction time | Yield of product II, % of theoretical |
|---|---|---|---|---|
| 1 | 1 drop HCl | 20 | 5 Hours | 52.2 |
| 2 | 2 drops HCl | 20 | Month | 54.5 |
| 3 | 1 drop HCl; hydroquinone | 70 | 5 Hours | 45.1 |
| 4 | 2% KOH | 80 | 6 » | 58.8 |
| 5 | 0,5% Nitrile | 80 | 6 » | 99.2 |
| 6 | 0,5% » | 20 | Month | 94.0 |
| 7 | None | 80 | 6 Hours | 90.9 |
| 8 | 0,5%Nitrile with thiophenol | 20—70 | 1 » | 95.0* |

*Product III.

Condensation with maleic anhydride. Heating 12.6 g of the addition product of ethyl mercaptan and ethynylvinyl thioethyl ether (II) and 7.8 g of maleic anhydride in 35 ml of benzene at 130° for 10 hours gave 4.6 g (69.4% of theoretical) of phthalic anhydride, which melted at 130.5° (from petroleum ether) and did not depress the melting point of a pure sample. The literature reports m. p. 131.6° [8].

Found %: C 65.14, 64.94; H 2.93, 2.82. $C_8H_4O_3$. Calculated %: C 64.87; H 2.72.

From the benzene fraction we isolated ethyl mercaptan as 2,4-dinitrophenyl ethyl sulfide with m. p. 114°, a mixed melting point was not depressed. The literature reports m. p. 115° [9]. Phthalic anhydride was also obtained from product III.

## LITERATURE CITED

[1] W. Franke and K. Seeman, Germ. Fed. Rep. Patent 871006, 1953.

[2] M. F. Shostakovskii, A. V. Bogdanova and G. K. Krasil'nikova, Proc. Acad. Sci. USSR, 114, 1250 (1957).*

[3] M. F. Shostakovskii, A. V. Bogdanova and G. K. Krasil'nikova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1958, No. 6.*

[4] M. F. Shostakovskii, A. V. Bogdanova and G. K. Krasil'nikova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 1141.*

[5] W. Franke, K. Weissbach, W. Dietrich and H. Weber, Germ. Patent 859 307, 1952.

[6] M. F. Shostakovskii and E. N. Prilezhaeva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 517.*

[7] M. F. Shostakovskii, E. N. Prilezhaeva and N. I. Uvarova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 526.*

[8] Dictionary of Organic Compounds, 3, 1949, p. 475.

[9] V. Hickbottom, Reactions of Organic Compounds, 1939, p. 169. [Russian Translation].

N. D. Zelinskii Institute of Organic Chemistry
Acad. Sci. USSR

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# INVESTIGATION OF THE PRECIPITATION OF HEXAVALENT URANIUM HYDROXIDE

S. A. Brusilovskii

(Presented by Academician D. S. Korzhinskii, January 7, 1958)

When examining the origin of uranium ore deposits and planning prospecting operations, using the hydrochemical method, it is necessary to know the conditions under which uranium compounds precipitate from various types of natural water. The most important forms for precipitation are the hydroxides, as the uranium minerals, which are the most common and the most valuable, from the industrial point of view, are those in the oxide group: uranite, pitchblende and uranium blacks which separate from aqueous solutions at low temperatures and inevitably pass through a hydroxide stage. This paper gives the results of investigations, completed in 1955, on the conditions of precipitation of hexavalent uranium hydroxide.

A series of papers [1-15] have examined the hydrolysis of the uranyl ion and its precipitation from solutions with alkalis. Various hydrolysis schemes with the participation of $UO_2OH^+$ [3, 14], $U_2O_5^{2+}$ [2] ions and other polymers with n = 3 [5, 9], n = 4 [4], up to n = 6 [10] were proposed. The number of hydroxyl groups in a polymer ion varies from 0 to 5 and the ion charge from +2 to −3. There is also considerable disagreement in the evaluation of the solubility product $L_{UO_2(OH)_2}$ from $7.4\cdot10^{-12}$, corresponding to the solubility of $S_{UO_2(OH)_2} = 0.16$ g/liter [16], to $2\cdot10^{-23}$ [17].

Let us establish a relation between the pH value at which hydroxide precipitation starts, the solubility product, and the initial concentration of metal ions in the solution. Taking into consideration the formation of soluble basic salts at the first hydrolysis stage, we have

$$Me^{n+} + m\,OH^- \rightleftarrows Me\,(OH)_m^{(n-m)+};\ Me\,(OH)_m^{(n-m)+} + (n-m)\,OH^- \rightleftarrows Me(OH)_n$$

Then the solubility product, corresponding to the actual dissociation scheme, equals

$$L_1 = [Me(OH)_m^{(n-m)+}]\,[OH]^{\,n-m}\,\gamma_{Me(OH)_m^{(n-m)+}}\,\gamma_{OH^-}^{n-m} \quad (1)$$

Using the expression for the ionic product of water:

$$K_B = [H^+]\,[OH^-]\,\frac{\gamma_{H^+}\gamma_{OH^-}}{a_{H_2O}} = K_B\,\frac{\gamma_{H^+}\gamma_{OH^-}}{a_{H_2O}}. \quad (2)$$

Introducing ionic indexes and substituting the value $[OH^-]\,\gamma_{OH^-}$ from (2) in (1), we obtain:

$$\begin{aligned} pL_1 = {} & p\,Me(OH)_m^{(n-m)+} - (n-m)\,pH + (n-m)\,p\,K_B - \\ & - \lg \gamma_{Me(OH)_m^{(n-m)+}} - (n-m)\lg(\gamma_{H^+}\gamma_{OH^-}). \end{aligned} \quad (3)$$

The solubility of the hydroxide $S = [Me(OH)_m^{(n-m)+}] = \frac{1}{n-m}[OH^-]$ is readily derived from (3):

$$pS = \frac{1}{n-m+1}[pL_1 + (n-m)\lg(n-m) + \\ + \lg\gamma_{Me(OH)_m^{(n-m)+}} + (n-m)\lg\gamma_{OH^-}]. \quad (4)$$

The "full" solubility product $L_2 = [Me^{n+}][OH^-]^n \gamma_{Me^{n+}}\gamma_{OH^-}^n$ has in this case only a formal value and may be referred as S:

$$L_2 = n^n S^{n+1}\gamma_{Me^{n+}}\gamma_{OH^-}^n. \quad (5)$$

Taking logarithms and substituting pS from (4) and then pL (1) from (3), after collecting similar terms we obtain:

$$pL(2) = \frac{1}{n-m+1}[(n+1)\,p\,Me(OH)_m^{(n-m)+} - (n-m)(n+1)\,pH + \\ + (n-m)(n+1)\,pK_B - (n-m)(n+1)\lg(n-m) - n(n-m+1)\lg n - \\ - (n-m+1)\lg\gamma_{Me^{n+}} - m\lg\gamma_{OH^-} - (n-m)(n+1)\lg(\gamma_{H^+}\gamma_{OH^-})]. \quad (6)$$

According to equation (3), in order to find $L_1$ and $L_2$, it is necessary to: a) establish the value m, which is determined by the actual hydrolysis scheme; b) establish experimentally the equilibrium pH at which precipitation starts, and c) use the values $\gamma_{Me^{n+}}$, $\gamma_{Me(OH)_m^{n-m+}}$ and $f = (\gamma_{H^+}\gamma_{OH^-})$. The initial concentration of metal ions and the ionic product of water are set by the experimental conditions.

Method. The main experimental method was potentiometric titration of perchlorate solutions of uranyl salts with NaOH solutions with pH measured by a glass electrode. The uranyl perchlorate solutions were prepared by dissolving $UO_3 \cdot 1.96\ H_2O$, purified by the peroxide method, in $HClO_4$. The alkali solutions, which did not contain carbonates, were prepared by dissolving metallic sodium in degassed, doubly distilled water (pH 6.5-6.8). The titration was carried out in a current of nitrogen, free from $CO_2$ and $O_2$, in a closed vessel placed in a mixer, imitating the movement of a hand during titration.

The relation of the pH at the beginning of hydroxide precipitation to the initial uranium concentration. The first series of titrations of $UO_2(ClO_4)_2$ from 0.1 to 0.00001 M was carried out by the usual method.

The curves obtained (Fig. 1) are close to the data found by Sutton [5] and many other authors, though we did not observe the constancy of the ratio $[OH^-] / [UO_2^{2+}]$, according to Sutton, which equals 1.66 for all concentrations and this indicates the inaccuracy of the hydrolysis scheme he proposed. We found that starting from a ratio of $[OH^-] / [UO_2^{2+}] > 1$, the equilibrium in uranyl salts being titrated with alkali is established slowly (after hours and days) so that ordinary titration with minute counts could not be used. Therefore, the following method was used. A certain volume of $UO_2(ClO_4)_2$ solution was poured into a series of test tubes and then alkali was added in such amounts that the ratio $[OH^-] / [UO_2^{2+}]$ changed from 0 in the first to 3.0 in the last tube; after this the tubes were stoppered and shaken at 20° for the required time, while their pH was periodically tested and precipitation watched for. Figure 2 shows the data obtained for 0.1 M starting solution. The same character was observed for the changes in other concentrations. Apparently, time "develops" the titration curve and brings out clear horizontal sections which correspond to the precipitation of uranyl hydroxide and its conversion to sodium diuranate. The usual titration curves (see Fig. 1) have sections which correspond to metastable phases. Figure 3 shows how the precipitation conditions change in relation to the initial uranium concentration. Up to the start of precipitation, the solution contains only monocharged uranium ions, i.e., m = 1.

Determination of the activity coefficients of the ions. As the only literature data we came across were those of Robinson and Lim [18], which, according to the activity coefficients, referred to more concentrated

uranyl salt solutions, we determined these coefficients ($\gamma_{UO_2^{2+}}$ and $\gamma_{UO_2OH^+}$) experimentally. If uranyl hydroxide precipitated in the absence of complex formers in two solutions with the same uranium concentration and with different ionic strengths, $\mu_1$ and $\mu_i$, then the pH at the start of precipitation would be different due only to the different activity coefficients. From equation (1) we have:

$$\lg \gamma_{UO_2OH^+_{(\mu_i)}} = \lg \gamma_{UO_2OH^+_{(\mu_1)}} + \Delta p\,[UO_2OH^+]_{(\mu_i-\mu_1)} - \Delta pH_{(\mu_i-\mu_1)} - \\ - \Delta \lg (\gamma_{H^+}\gamma_{OH^-})_{\mu_i-\mu_1}. \qquad (7)$$

An analogous expression may be obtained for $\gamma_{UO_2^{2+}}$. If $\mu_1$ is quite small then the first term in equation (7) may be calculated by the Debye-Hückel formula, the second term is set by the experimental conditions (dilution), ΔpH is determined experimentally and the 4th term is calculated from table data. One can show that the curves for potentiometric titration of uranium solutions with different ionic strengths are equidistant, so that the experimental determination of $\gamma_{UO_2OH^+}$ and $\gamma_{UO_2^{2+}}$ is reduced to potentiometric titration of a uranyl perchlorate solution, neutralized before the start of hydroxide precipitation, with an $NaClO_4$ solution, which changes the ionic strength. By this method we obtained the data shown in Fig. 4.


Fig. 1. Curves for the potentiometric titration of $UO_2(ClO_4)_2$ solution with sodium hydroxide, plotted in the usual way. The uranium concentration was $C_{UO_2^{2+}}$: A) 0.1 M, B) 0.01 M, C) 0.001 M, D) 0.0001 M, E) 0.00003 M, F) 0.00001 M. Sutton's data are shown with crosses (0.01 M); the arrows indicate the start of visible precipitation.

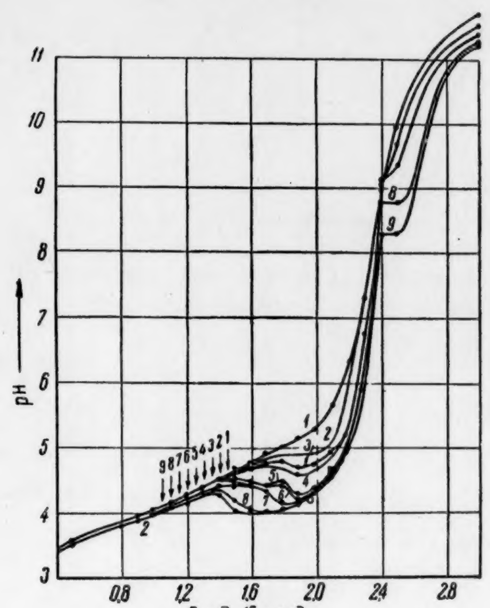


Fig. 2. Changes in the curves for the potentiometric titration of a 0.1 M $UO_2(ClO_4)_2$ solution with sodium hydroxide with time 1) t = 0; 2) curve A Fig. 1, t = 2 min; 2) t = 1 day; 4) t = 3 days; 5) t = 6 days; 6) t = 8 days; 7) t = 13 days; 8) t = 60 days; 9) t = 107 days; the arrows indicate the start of visible precipitation.

Determination of the solubility product of uranyl hydroxide. By substituting the data obtained in equations (1) and (3), we calculated the following for uranyl hydroxide: $L_1 = 1.3 \cdot 10^{-11}$, $L_2 = 6 \cdot 10^{-18}$ and $S = 3.3 \cdot 10^{-4}$ g/liter ($\mu < 0.001$) at t = 20°. Direct determination of $SUO_2(OH)_2$ give high results [16] due to the exceptional tendency of the hydroxides to form colloidal solutions. The displacement of the pH the start of hydroxide precipitation due to temperature change determined to discover the temperature dependence of $L_{UO_2(OH)_2}$, and $L_{ti}$ was calculated from the equation derived from (1):

$$pL_{1t_2} = pL_{1t_1} + \Delta pH - \Delta pK_B + \Delta \lg \gamma_{UO_2OH^+} + \Delta \lg (\gamma_{H^+}\gamma_{OH^-}). \quad (8)$$

The temperature dependence of L (2) was determined analogously. These relations are expressed by the equations:

$$pL_1 = 12.16 - 0{,}0141\,t. \quad (9)$$
$$pL_2 = 17.65 - 0.2156\,t. \quad (10)$$

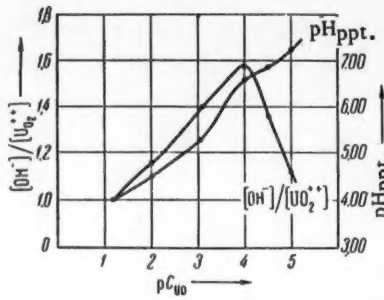


Fig. 3. The relation of the conditions of $UO_2(OH)_2$ precipitation to uranium concentration.

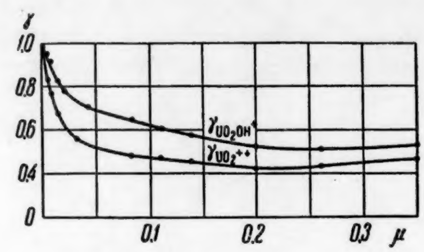


Fig. 4. The relation of the activity coefficients of $UO_2OH^+$ and $UO_2^{2+}$ to the ionic strength of the solution.

The data obtained in the work make it possible to calculate the conditions of hexavalent uranium precipitation from some types of natural waters.

## LITERATURE CITED

[1] H. T. S. Britton, J. Chem. Soc. (London) 127, 2148 (1925).

[2] H. Guiter, Bull. Soc. Chim. France (5), 13, 4034 (1946); (5), 14, 275 (1947).

[3] W. E. Harris and J. M. Kolthoff, J. Am. Chem. Soc. 69, No. 7, 1175 (1947).

[4] J. S. Anderson, Nature, 163, 983 (1949).

[5] B. J. Sutton, J. Chem. Soc. 1949, 275.

[6] S. Ahrland, Acta Chem. Scand. 3, 374 (1949).

[7] G. Tridot, Ann. Chim. (12) 5, 358 (1950).

[8] C. Tanford, R. L. Tichenoe and H. A. Young, J. Am. Chem. Soc. 73, 4491 (1951).

[9] C. A. Wamser, J. Belle, E. Bernsohn and B. Williamson, J. Am. Chem. Soc. 74, 1020 (1952).

[10] S. Ahrland, S. Hietanen and L. G. Sillen, Acta Chem. Scand. 8, No. 10, 1907 (1954).

[11] K. H. Gayer and H. Leider, J. Am. Chem. Soc. 77, 1448 (1955).

[12] B. J. Sutton, J. Inorg. and Nucl. Chem. 1, No. 1-2, 68 (1955).

[13] J. E. Picci and F. J. Lopest, J. Am. Chem. Soc. 77, 2119 (1955).

[14] N. P. Komar' and V. A. Tret'iak, J. Anal. Chem. 10, No. 4, 236 (1955).*

*Original Russian pagination. See C. B. Translation.

[15] B. P. Nikol'skii, V. N. Paramonova and M. D. Morachevskaia, J. Inorg. Chem. 2, No. 5, 1194 (1957). *

[16] J. Katz and E. Rabinovich, Chemistry of Uranium, 1, Foreign Lit. Press, 1954 [Russ. Translation].

[17] V. M. Latimer, Oxidation States of Elements and Their Potentials in Aqueous Solutions, Foreign Lit. Press, 1954 [Russ. Translation].

[18] R. A. Robinson, C. K. Lim, J. Chem. Soc. 1951, 1840.

Institute of Geology of Ore Deposits, Petrology,
Minerology and Geochemistry
Academy of Sciences USSR

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* In Russian.

# THE FORM IN WHICH SILICON EXISTS IN LIQUID IRON

A. A. Vertman and Corresponding Member Academy of Sciences
USSR A. M. Samarin

One of the least studied problems is that of the form in which elements exist when dissolved in liquid metals, although it is important in the theory of the liquid state and from the practical point of view in the metallurgical industry. This is due to the difficulties of performing experiments at high temperatures and, mainly, to the fact that the majority of the investigators tackled the problem from the point of view of formal thermodynamics. An example of this is Darken's paper [1], in which he concluded that silicon is present in a melt in the form of the $Fe_3Si$ molecule, partially dissociated into atoms. However, the calculated value for the solution heat of silicon in iron [1] contradicts the direct thermodynamic measurements.

Data on the structure of liquid metals and their alloys may be obtained by x-ray analysis [2] or indirectly from data on solubility of gases and separate elements in a liquid metal [3]. X-ray analysis of a liquid at high temperatures and over a wide range of temperatures is very difficult experimentally and is by no means free from systematic errors, which make interpretation of the results obtained difficult; due to this, conclusions on the characteristics of this or that structure of metallic melts are not unequivocal [4]. A simpler way of studying the structure of metallic melts, which is equally reliable, is to measure their structural-sensitive properties – electroconductivity, viscosity and magnetic susceptibility. These properties may be measured by non-contact methods, which is a deciding factor in investigations at high temperatures.

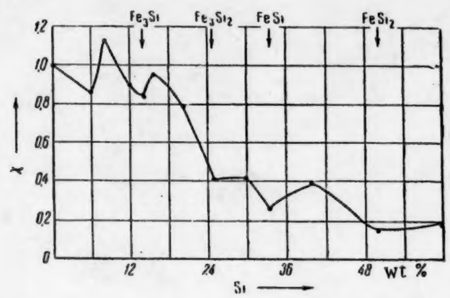


Fig. 1. Change in magnetic susceptibility of liquid melts of the Fe-Si system at 1600° in relation to composition.

In order to establish the forms in which silicon is present in liquid iron, we measured the magnetic susceptibility of liquid alloys of the Fe-Si system (from 0 to 60 weight % of Si).

The measurements were carried out by Faraday's method on a special apparatus [5]. The results of measurements at 1600° are given in relative units in Fig. 1. They indicate that the magnetic susceptibility $\underline{x}$ is much lower, the higher the degree of order in the solution. Actually, a minimum in $\underline{x}$ was noted for melts containing 34% silicon and corresponding to the stable chemical compound FeSi. This iron silicide is stable even in the temperature range of steel working (1500-1700°).

The presence of FeSi was also confirmed by the results of determining other characteristics of iron and silicon melts. The value of the e.m.f. changes radically in the Fe-Si-C system with 32.5% silicon [6]. In determining the surface tension of the Fe-Si system [7] and the interphase tension at the FeSi-slag boundary [8], an experimental point was found which corresponded to the melt containing 34% silicon. The FeSi compound is apparently so stable that its presence is detected even by relatively crude measurements, which do not indicate the presence of other structural forms in Fe-Si melts.

It was noted [9, 10] that the Kurnakov point, characterizing the conversion order-disorder, in melts of the Fe-Si system, and in a melt of iron aluminum and silicon, lies close to the melting point, and possibly, above it. In fact, a definite degree of order, which is, apparently, quite high, is maintained even on superheating the melts containing 12-16% silicon, to 150° above the liquidus line.

It seemed interesting to compare the results of the magnetic analysis, which reflected the structural changes in the liquid in relation to composition, with the chemical properties of the melts. According to the data available [3], all the isotherms up to 1650° for hydrogen solubility at atmospheric pressure have a clearly defined minimum at 34 wt. % of silicon, which corresponds to the minimum of magnetic susceptibility. It was shown [11] that the curve of nitrogen solubility at 1600° in iron and silicon melts in relation to the composition passes through a minimum at a 13-15% silicon content, which also corresponds to a minimum in magnetic susceptibility. With an increase in the silicon content to 20% the nitrogen solubility rises as does the magnetic susceptibility.

## SUMMARY


1. The magnetic susceptibility of Fe-Si system melts have a minimal value for compositions corresponding to the chemical compounds: $Fe_3Si$; $Fe_3Si_2$; FeSi and $FeSi_2$ – which is direct proof of the presence of structural forms similar to silicides, in the melts.

2. The magnetic susceptibility of the melts decreases with an increased degree of order. It is minimal for chemical compounds and maximal for solutions with completely mixed atoms.

3. The structural changes in the melts are related to their chemical properties, in particular to the solubility of gases.


## LITERATURE CITED


[1] L. Darken, Trans. AIMME, 140, 204 (1940).

[2] V. I. Danilov, The Structure and Crystallization of Liquids, 1956.*

[3] O. A. Esin and P. V. Gel'd, Physical Chemistry of Pyrometallurgical Processes, Pt. II, 1954.*

[4] I. V. Radchenko, Prog. Phys. Sci. 61, No. 2, 249 (1957).

[5] A. A. Vertman and A. M. Samarin, Indust. Lab. No. 3, 109 (1958).**

[6] O. A. Esin and L. K. Gavrilov, Bull. Acad. Sci. USSR, Div. Tech. Sci. 8, 1234 (1951).

[7] P. V. Gel'd, N. V. Zaimskikh, N. N. Serebrennikov and Iu. P. Nikitin, J. Appl. Chem. 25, 687 (1952).**

[8] P. V. Gel'd, S. I. Popel' and Iu. P. Nikitin, J. Appl. Chem. 25, 592 (1952).**

[9] F. Glaser and W. Ivanick, J. Metals, 10, 1290 (1956).

[10] R. Garrold and L. Hogan, Acta Metal. 2, 6, 886 (1954).

[11] A. M. Samarin and V. P. Fedotov, Rept. to the 4th Conf. on the Phys.-Chem. Bases of Steel Manufacture, 1957.*



A. A. Baikov Institute of Metallurgy
Academy of Sciences USSR



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* In Russian.

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# THE EFFECT OF ATOMIC CONCENTRATIONS OF CHROMIUM, MOLYBDENUM AND TUNGSTEN ON THE PROPERTIES OF NICKEL SOLID SOLUTIONS

I. I. Kornilov and N. T. Domotenko

(Presented by Academician A. A. Blagonravov, January 11, 1958)

Chromium, molybdenum and tungsten, elements of group VI of the periodic table, have a body-centered cubic lattice and form limited solid solutions with nickel.

The solubility of these elements in nickel decreases in the order chromium, molybdenum and tungsten. It is determined by the relative differences in the atomic diameters of nickel and these metals. The difference between the atomic diameters of these elements and the atomic diameter of nickel, and their maximum solubility in nickel are the following:

| | Cr | Mo | W |
|---|---|---|---|
| Difference between at. diameters and at. diameter of Ni (in %) | 3 | 12.4 | 13.3 |
| Maximum solubility (in at. %) | | | |
| at the eutectic point | 50.0 | 23.0 | 18.1 |
| at 700° | 40.0 | 14.9 | 13.0 |

The substitution of the metal-solvent atoms by atoms of the dissolved substance causes the formation of additional chemical bonds in the system, which strengthen the lattice of the metal-solvent. This was pointed out in a paper [1] on the physicochemical theory of the heat stability of solid metal solutions.

The different solubilities of chromium, molybdenum and tungsten in nickel and the differences in their atomic structures, as well, must have different effects on the properties of nickel solid solutions. This paper aims at establishing the rules governing the changes in these properties in relation to the atomic concentration of Cr, Mo and W, using physicochemical analysis. The results of measuring the lattice period of a nickel solid solution showed that at equal atomic concentrations of these elements, the degree of deformation of the nickel crystal lattice increased from Cr to Mo and W. This order corresponds to the sequence of these elements in the periodic table and is a result of the degree to which their atomic diameters differ from the atomic diameter of nickel. This is confirmed by the different degree of expansion of the nickel lattice parameter at equal atomic concentrations of Cr, Mo and W (Table 1).

TABLE 1

Lattice Parameters of Pure Ni and Its Solid Solutions with 4, 6 and 10 at. % of Cr, Mo and W

| | Lattice parameter A | | Lattice parameter A | | Lattice parameter A |
|---|---|---|---|---|---|
| Ni | 3.518 | with Cr 6 % | 3.524 | with Cr 10 % | 3.528 |
| Ni solid solutions: | | with Mo 6 % | 3.542 | with Mo 10 % | 3.558 |
| with Cr 4 % | 3.522 | with W 6 % | 3.543 | with W 10 % | 3.560 |
| with Mo 4 % | 3.533 | | | | |
| with W 4 % | 3.535 | | | | |

TABLE 2

Hardness of Ni Alloys with 4, 6 and 10 at. % of Cr, Mo and W (in kg /mm²)

| Temperature, °C | Cr | | | Mo | | | W | | |
|---|---|---|---|---|---|---|---|---|---|
| | 4% | 6% | 10% | 4% | 6% | 10% | 4% | 6% | 10% |
| 20 | 96 | 102 | 124 | 124 | 144 | 166 | 106 | 120 | 142 |
| 800 | 40 | 46 | 60 | 82 | 98 | 122 | 72 | 84 | 110 |
| 1000 | 20 | 22 | 26 | 42 | 51 | 64 | 30 | 36 | 42 |

As these data show, the greatest difference in the lattice parameters occurred in the case of a nickel solid solution with tungsten (at 4, 6 and 10% concentrations of W) and the least – in nickel solid solutions with chromium (with the same concentrations of Cr). Molybdenum occupied an intermediate position.

A study of the specific electrical resistance with the same atomic concentrations of Cr, Mo and W showed that the sequence of growth of this physical constant was also in the order, chromium to molybdenum to tungsten. Using alloys with 4, 6 and 10% Cr, Mo and W, we then studied their hardness at room temperature, at 800 and 1000° (see Table 2) and their heat stability at 800° and a pressure of 4 kg/mm² and at 1000° and a pressure of 2 kg/mm². The hot hardness was studied on the apparatus described in paper [2], while the heat stability was tested by the bending method on a centrifugal machine [3].

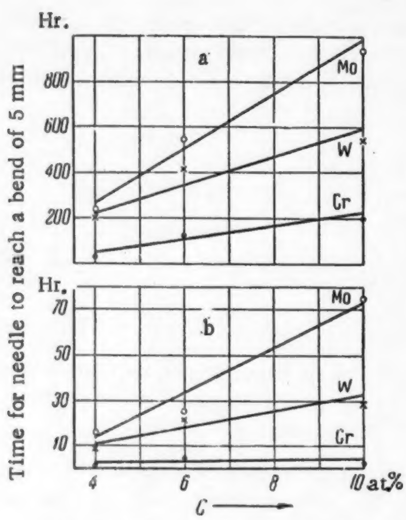


Fig. 1. The relation of the time required for the needle to reach a bend of 5 mm to the Cr, Mo and W content of a nickel solid solution. a) at t = 800°C, $\sigma$ – 4 kg/mm², b) at t = 1000°C, $\sigma$ = 2 kg/mm².

As the data in Table 2 show, the hardness values at equal atomic concentrations and at the temperatures investigated increased from chromium to tungsten to molybdenum. Molybdenum gave the maximum increase in hardness of nickel solid solutions at all three temperatures. Thus, for change in hardness, as one of the characteristics of stability, the sequence of the effect of Cr, Mo and W does not correspond to their position in the periodic table. The same was observed in the changes in heat stability (determined by the bend method) in relation to concentration of these metals in solid solutions with nickel. Using the results of measuring the bend of the needle after various periods of pressure, we plotted a diagram showing the time required for the needle to reach a bend of 5 mm in relation to the Cr, Mo and W content of nickel solid solutions. The corresponding curves for 800 and 1000° are given in Fig. 1. An analysis of this graph shows that an increase in Cr, Mo and W concentrations in a nickel solid solution resulted in a strengthening of the alloys at both the isotherms given in the graph. With equal atomic concentrations of the effective element, alloys of nickel and molybdenum have a higher value for heat stability than the solid solutions with chromium and tungsten. At a temperature of 800° and a pressure of 4 kg/mm² for the needle to reach a bend of 5 mm, a Ni solid solution with 10 at. % of Cr required 200 hours, with 10% W – 500 hours and with 10% Mo – more than 900 hours.

The results of these investigations are summarized in a diagram (Fig. 2), in which the elements interacting with nickel are plotted on the abscissa in the order in which they appear in group VI of the periodic table, and the time required for the needle to reach a bend of a given amount (5 mm) in determining the heat stability at 800°C and a pressure of 4 kg/mm², is plotted on the ordinate. This diagram shows that at all three concentrations of the elements reacting with Ni investigated, the heat stability of the solid solutions of Cr, Mo and W changes in the same sequence as hardness at the same temperature. According to the value of heat stability, as with hardness, these elements may be placed in the order: Cr — W — Mo.

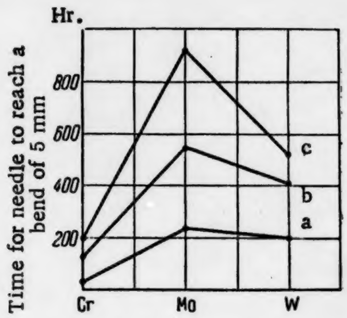


Fig. 2. The effect of chromium, molybdenum and tungsten on the stability of a nickel solid solution at t = 800°C and $\sigma$ = 4 kg/mm². a) C = 4 at. %, b) C = 6 at. %, c) C = 10 at. %.

The difference in the effect of molybdenum and tungsten on the electrical resistance and on the change in the crystal lattice period of the solid solution, on the one hand, and on hardness and heat stability, on the other, may be explained by the fact that the difference in atomic diameters has a decided effect on the first two properties, while the strength of the chemical bond between the reacting atoms in the solid metal solutions affects the mechanical properties. In the last case, the elements affect the chemical strengthening of nickel solid solutions individually.

A decrease in the heat stability of alloys when tungsten replaces molybdenum in a nickel solid solution is probably due to the fact that the strength of the chemical bond between nickel and tungsten atoms is less (due to the more complicated structure of tungsten atoms) than between nickel and molybdenum. These problems require further investigation.

## LITERATURE CITED

[1] I. I. Kornilov, Proc. Acad. Sci. USSR 67, No. 6, 1037 (1949).

[2] M. G. Lozinskii, High-Temperature Metallography, 1957.*

[3] I. I. Kornilov, Bull. Sec. Phys.-Chem. Analysis, 72, 1 (1949).

N. R. Zhukovsky Air Force Academy of Engineering

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* In Russian.

# THE EFFECT OF $\gamma$-RADIATION ON COAL IN AN AQUEOUS MEDIUM AND IN A CARBON TETRACHLORIDE MEDIUM

B. I. Losev, M. A. Troianskaia and E. A. Bylyna

(Presented by Academician A. V. Topchiev, January 13, 1958)

It is known from papers on water radiolysis [1, 2] that, under the effect of ionizing radiation, ions and free radicals are formed in water in the presence of atmospheric oxygen, and these are capable of causing the oxidation or reduction of substances, added to the aqueous system irradiated. One might expect that $\beta$-radiation of coal in an aqueous medium would induce chemical changes in the most reactive part of the organic substance of coal and the transfer of the germanium, contained in the coal, to the aqueous medium. The use of the oxidative processes, occurring during the irradiation of an aqueous medium, would be valuable not only for extraction of germanium, but also for investigating and identifying the products of the radiolytic purification of coal.

We irradiated coal in an aqueous medium in glass ampules with a dose strength of 200 r/sec and an integral dose of $10^8$ r. $Co^{60}$ was the $\gamma$-radiation source.

For the investigations we used four grades of coal: lignite from the basin near Moscow and coal from the Donets basin—bituminous steam coal (BS), gas coal (G) and coke (C). The germanium content of the latter two grades was very low.

After irradiation the coal was filtered from the water and the aqueous medium analyzed for germanium content. The germanium was determined using the method developed by the Ukrainian Institute of Rare Metals. The determination results are given in Table 1.

TABLE 1

| | Sample, g | | Germanium yield | |
|---|---|---|---|---|
| | coal | water | $\gamma$ per g of coal | % of coal content |
| Lignite from near Moscow | 5 | 25 | 2.26 | 41.0 |
| BS coal | 3 | 21 | 1.6 | 50.2 |
| G coal | 5 | 25 | 0.18 | 5.8 |
| Coke (c) | 5 | 20 | 0.16 | 13.3 |

The largest germanium yields from the irradiation of coal in an aqueous medium were obtained from the BS grade of coal (50.2%) and the lignite (41.0%).

We further investigated the possibility of increasing the germanium yield from coal by using chlorination, which is one of the most important, from the theoretical and also from the practical point of view, of a group of methods for extracting rare and dispersed elements from minerals, polymetallic ores [3] and from coal [4, 5].

Elemental chlorine is mainly used in the chlorination. The use of such strongly chlorinating chlorine compounds as sulfur monochloride, carbon tetrachloride etc. can considerably increase the possibilities of this method.

Many papers on radiation chemistry [6-8] report that free chlorine is the main radiolysis product when carbon tetrachloride is irradiated with $\gamma$-rays. We made use of this phenomenon in our work on extracting germanium from coal in carbon tetrachloride. Coal samples in carbon tetrachloride were placed in molybdenum glass ampules and sealed in an atmosphere of air. The irradiation was carried out at three different integral doses: $10^6$, $10^7$ and $10^8$ r. The dose strength was 200 r/sec in all cases.

After irradiation the ampules were opened, the coal separated from the liquid phase,and the germanium content both of the liquid phase and of the coal was determined to obtain a complete balance for the germanium.

Very little germanium passed into the liquid phase in grade G coal and coke (C) at integral radiation doses of $10^6$ and $10^7$ r. At $10^8$ r integral dose, the germanium yield from coke was 13% and from gas coal – only 5.6% of the total amount of the element in the coal.

A higher germenium extraction index of up to 53% was obtained on irradiating grade BS coal. Table 2 gives the experimental results of irradiating dried, grade BS coal in dry carbon tetrachloride.

We obtained complete extraction of the germanium by irradiating dried lignite in dry carbon tetrachloride (see Table 2).

TABLE 2

| | Integral radiation dose, r | Germanium yield | |
|---|---|---|---|
| | | $\gamma$ per g of coal | % of coal content |
| BS coal from the Donets basin | $10^6$ | 0.24 | 7.5 |
| | $10^7$ | 0.97 | 30.0 |
| | $10^8$ | 1.70 | 53.0 |
| Lignite from near Moscow | $10^6$ | 0.2 | 2.9 |
| | $10^7$ | 1.2 | 17.4 |
| | $10^8$ | 6.9 | 100.0 |

At an integral dose of $10^8$ r all the germanium in the coal passed into the liquid phase, from which it could be extracted by existing methods.

The degree of extraction of germanium from coal depended not only on the radiation dose, but also on the presence of moisture in the system. When dried lignite was irradiated in undried carbon tetrachloride, the germanium yield decreased to 40.3%. Irradiation of moist lignite (14% moisture) in undried carbon tetrachloride with the same integral dose, gave a germanium yield of only 9.3%. Irradiation of grade BS coal gave analogous results. Irradiation of dried BS coal in dry carbon tetrachloride gave a germanium yield of 53%, while in undried carbon tetrachloride the germanium yield fell to 12.4%. Irradiation of undried BS coal in moist carbon tetrachloride with the same integral dose ($10^8$ r) gave a germanium yield of only 6% of the total content.

Besides using carbon tetrachloride radiolysis for extracting germanium from coal, we observed an increased solubility of coal in carbon tetrachloride after $\gamma$-irradiation which, without doubt, could be very valuable from the point of view of the chemical processing of coal.

## LITERATURE CITED


[1] P. I. Dolin, Coll. Work on Radiation Chemistry, Acad. Sci. USSR Press 1955, p. 7, 24.

[2] V. I. Veselovskii, Ts. I. Zalkin, N. B. Miller and N. A. Aladzhalova, Work on Radiation Chemistry, Acad. Sci. USSR Press, 1955, p. 36.

[3] A. A. Cherepnev, Problems on the Chlorination of Rare Dispersed Elements, 1940.*

[4] B. I. Losev, A. N. Mel'nikova and I. E. El'piner, Bull. Acad. Sci. USSR, Div. Tech. Sci. No. 9 (1957).

[5] B. I. Losev, I. E. El'piner and A. N. Mel'nikova, Proc. Acad. Sci. 114, No. 2, 372 (1957).**

[6] A. V. Zimin and Z. S. Egorova, Coll. Work on Radiation Chemistry, Acad. Sci. USSR Press, 1955, p. 241.*

[7] J. W. Schulte, J. F. Suttle and R. J. Wilhelm, J. Am. Chem. Soc. 75, 2222 (1953).

[8] P. Günther, H. D. Horst and G. Cronheim, Zs. Elektrochem. 34, 616 (1928).



Institute of Combustible Minerals
Academy of Sciences USSR



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# DISPROPORTIONATION OF HYDRAZO COMPOUNDS ON HEATING WITH AMINE SALTS AND WEAK ACIDS

V. O. Lukashevich and L. G. Krolik

(Presented by Academician B. A. Kazanskii, January 22, 1958)

It is well known that the hydrazo compounds of the benzene series slowly decompose to form almost exclusively disproportionation products, when gently heated (100-150°) in an inert medium.* According to our determinations, if an equimolecular amount of azobenzene is added to hydrazobenzene, to keep it in a molten state, and this mixture is heated at 110°, after 60 min. the hydrazobenzene disproportionation will be only 7% of the theoretical, as shown by the amount of aniline formed. 2,2'-Dimethylhydrazobenzene decomposes much more slowly in the presence of an equimolecular amount of the corresponding azo compound. Isomeric 3,3'- and 4,4'-dimethylhydrazobenzenes (ligroin was added to the latter) decompose almost as rapidly as hydrazobenzene. The disproportionation of these hydrazo compounds corresponds to 1, 4.8 and 10.4% of the theoretical, respectively (see Table 1).

We have now established that in the presence of hydrochlorides of amino compounds, disproportionation of hydrazo compounds accelerates sharply. Thus, for example, on heating (110°) a finely ground mixture of equimolecular amounts of hydrazobenzene and aniline hydrochloride, the mass rapidly became red and melted and after only 15 min the hydrazobenzene disproportionation reached 80%; the reaction mixture was a bright, reddish color and only traces of o-aminodiphenylamine were found in the rearrangement products.

When the amount of aniline hydrochloride was decreased to 10% of molar, the hydrazobenzene decomposed more slowly; nevertheless, after heating for an hour somewhat more than 80% had decomposed (experiment No. 2 in Table 1). With stronger heating (140-160°) the partially resinified mass contained considerably greater amounts of rearrangement products—among them benzidine (about 2%).

The effects of benzidine dihydrochloride and aniline hydrochloride on hydrazobenzene were almost identical, but benzidine monohydrochloride had a much weaker effect (experiment No. 5 in Table 1) which is explained by the weaker dissociation of this salt, due to the high basicity of benzidine. Using the fact that benzidine, aniline and benzidine hydrochloride are a series of compounds with successively decreasing basicity, we were able to obtain monohydrochlorides of benzidine and analogs, that are difficultly obtainable, by treating the dihydrochlorides of these bases in aqueous solutions with aniline; the yields were over 85-90% of the theoretical.

The mechanism of the reaction described consists of the following: very small amounts of HCl, formed by weak dissociation of the amine hydrochlorides when gently heated, were trapped by the hydrazo compound and this resulted in the formation of the corresponding hydrochloride:

$$RNH - NHR + HCl \rightleftarrows |RNH - \overset{+}{N}H_2R|\overline{Cl}, \qquad (1)$$

which dissociates to a greater degree than the original amine hydrochlorides. Using hydrazobenzene hydrochloride as the example, we showed [2] that in an inert gas atmosphere and at normal temperature this

*As we showed under analogous conditions, rearrangement occurs in the naphthalene series [1].

TABLE 1

| Expt. No. | Initial substance | | Obtained | | Hydrazo compound recovered, % | Total of all substances, % |
|---|---|---|---|---|---|---|
| | Hydrazo compound (0.005 mole) | Amine salt or acid (0.0005 mole) | Mono-amine, % | azo compound, % | | |
| 1 | Hydrazobenzene | | 3.5 | — | — | — |
| 2 | | Aniline hydrochloride | 40.7 | 42.0 | 13.0 | 95.7 |
| 3 | | Aniline sulfate | 3.5 | — | — | — |
| 4 | | Benzidine dihydrochloride (0.00025 mole) | 39.6 | 40.8 | 17.0 | 97.4 |
| 5 | | Benzidine monohydrochloride | 28.0 | 27.7 | 39.7 | 95.4 |
| 6 | | Benzoic acid | 25.2 | 25.1 | 46.4 | 96.7 |
| 7 | | Acetic acid | 17.0 | 18.2 | 61.3 | 96.5 |
| 8 | | Butyric acid | 14.5 | 15.0 | 68.1 | 97.6 |
| 9 | 2,2'-dichlorohydrazobenzene | Aniline hydrochloride | 0.5 | 0.8 | 94.8 | 96.1 |
| 10 | 3,3'-dichlorohydrazobenzene | | 1.0 | 1.1 | — | — |
| 11 | | Aniline hydrochloride | 31.3 | 33.0 | 32.2 | 96.5 |
| 12 | 4,4'-dichlorohydrazobenzene | | 2.0 | 3.0 | — | — |
| 13 | | Aniline hydrochloride | 46.7 | 47.2 | 2.0 | 95.9 |
| 14 | 2,2'-dimethylhydrazobenzene | | 0.5 | — | — | — |
| 15 | | o-Toluidine hydrochloride | 34.0 | 35.0 | 27.4 | 96.4 |
| 16 | 3,3'-dimethylhydrazobenzene | | 2.4 | — | — | — |
| 17 | | Aniline hydrochloride | 41.1 | 42.8 | 12.1 | 96.0 |
| 18 | 4,4'-dimethylhydrazobenzene | | 5.2 | 5.6 | — | — |
| 19 | | Aniline hydrochloride | 46.5 | 48.7 | Traces | 95.2 |
| 20 | 2,2'-dimethoxyhydrazobenzene | | 14.5 | 15.5 | — | — |
| 21 | | o-Anisidine hydrochloride | 39.0 | 40.5 | 7.5 | 87.0 |

substance undergoes an oxidation-reduction which gives azobenzene and aniline; gentle heating accelerates this process considerably:

$$2\,|\,RNH-\overset{+}{N}H_2\,|\,\overline{Cl} \rightarrow RN=NR + 2\,|\,R\overset{+}{N}H_3\,|\,\bar{Cl}. \qquad (2)$$

Reactions (1) and (2) describe the formation of hydrazobenzene disporportionation products under the conditions interesting us.

In addition, it is also possible that hydrazobenzene hydrochloride reacts with HCl:

$$|\,RNH-\overset{+}{N}H_2R\,|\,\overline{Cl} + HCl \rightarrow \text{rearrangement products} \qquad (3)$$

and this would inevitably result in rearrangement products. However, with a very large reserve of excess hydrazo compound in the reaction mixture during almost the whole course of the process examined, considerable amounts of rearrangement products could be formed only at the very end, at the point when the hydrazo compound is exhausted. One can add as confirmation of the above the fact that according to experimental data, the rate of formation of hydrazobenzene monohydrochloride (1) was considerably greater than the rate of the subsequent rearrangement. In fact, according to our data (2), hydrazobenzene hydrochloride is obtained almost quantitatively on gradually adding an ether solution of HCl to an equimolecular amount of hydrazobenzene in ether.

If one takes into account the individual characteristics of other hydrazo compounds, one may consider that basically they are similar to those of hydrazobenzene (see Table 1).

TABLE 2

| Expt. No. | Initial substance: hydrazo compound (0.01 mole) | Initial substance: acid (15 ml) | Temperature °C | Duration of experiment | Obtained: monoamine,* % | Obtained: azo compound, % | Obtained: rearrangement products, % | Total of all substances, % |
|---|---|---|---|---|---|---|---|---|
| 1 | Hydrazobenzene | 98% Acetic | 18—20 | 10 Days | 14.0 | 15.6 | 60.5 | 90.1 |
| 2 | 4,4-dichlorohydrazobenzene | 35% Hydrochloric | 5—10 | 30 Min. | 17.0 | 20.1 | 58.2 | 95.3 |
| 3 | 2,2-dimethylhydrazobenzene | 98% Acetic | 18—20 | 10 Days | 6.2 | 6.4 | 76.0 | 88.6 |
| 4 | 4,4-dimethylhydrazobenzene | 98% Acetic | 18—20 | 1 Day | 33.5 | 34.6 | 19.9 | 88.0 |
| 5 | 2,2-dimethylhydrazobenzene | 100%Butyric | 2—20 | 1 Day | 25.0 | 26.2 | 35.0 | 86.2 |
| 6 | 4-ethoxyhydrazobenzene | 98% Acetic | 18—20 | 1 Day | 26.0 | 27.4 | Not deter. | — |

*The substance was dissolved in 15 ml of benzene and shaken with acid.

Similar results were obtained in the cases of 2,2'- and 3,3'-dimethylhydrazobenzenes (Experiments No. 15 and 17, Table 1). The more acid sensitive 4,4'-dimethylhydrazobenzene (Experiment No. 19) and, especially, 2,2'-dimethoxyhydrazobenzene broke down more rapidly. The latter compound was disproportionated relatively quickly even in the absence of salts; with the addition of o-anisidine hydrochloride the reaction mixture partially resinified and dianisidine was formed in addition to the disproportionation products (Experiment No. 21). The behavior of dichlorohydrazobenzenes should be considered: the 2,2'-isomer, which reacts with acids with the greatest difficulty, remained almost unchanged (Experiment No. 9); on the contrary, 4,4'-dichlorohydrazobenzene, which under normal conditions is much less sensitive to acids than, for example, hydrazobenzene, broke down almost completely (Experiment No. 13). Apparently, in the first case equilibrium [1] was very strongly displaced towards the left, so that there was practically no 2,2'-dichlorohydrazobenzene hydrochloride formed under the given conditions; in the second case 4,4'-dichlorohydrazo compound was broken down so completely due to the great rate of the oxidation-reduction conversion of the hydrazo compound hydrochloride formed (see Equation (2)), which, apparently, is characteristic of all hydrazo compounds with substituents in a position para to the hydrazo group.

Disproportionation of hydrazo compounds is also catalyzed by weak acids. We tried treating hydrazobenzene with benzoic [3] ($K_{dis}$ at 25° = $6.5 \cdot 10^{-5}$), acetic [4] ($K_{dis}$ at 25° $1.845 \cdot 10^{-5}$) and butyric [5] ($K_{dis}$ at $1.55 \cdot 10^{-5}$) acids in 0.1 mole amounts with respect to hydrazobenzene. We should note that at normal temperatures hydrazobenzene in glacial acetic acid was fully converted only after several days; anhydrous butyric acid had a much slower action. As could be expected, the greatest degree of disproportionation occurred in the presence of benzoic acid ( 50.4%), then acetic (34%) and butyric (29%) acids.

Undoubtedly in these cases the process also proceeded in two stages: the monoprotonized hydrazo compound formed did not have enough time for rearrangement under the effect of a weak acid and underwent an oxidation-reduction conversion, according to equation (2).

In connection with the above, we would like to point out how great is the disproportionation of some hydrazo compounds during rearrangement, in particular that of those compounds with substituents in a position para to the hydrazo group, many of which react readily with weak acids (see Table 2). 4,4'-Dichlorohydrazobenzene disproportionation was 34% even when concentrated hydrochloric acid was used (cf. [6]) and on dilution it increased sharply.

## EXPERIMENTAL

Disproportion of hydrazo compounds on heating. The reagents (see Table 1) in a tube under nitrogen were placed in a glycerin bath heated to 111-112° and left in it for 60 minutes, after which the tube was quickly cooled and extracted with benzene, to which a little ether had been added.

We then proceeded as follows. In the experiments with hydroazobenzene and the three isomeric hydrazotoluenes, the benzene-ether solution was cooled with ice and vigorously shaken for several seconds with a large excess of a 1% solution of hydrochloric acid, which was also cooled. After separation from the benzene layer, the acid solution was made alkaline and boiled; the amount of aniline or toluidine distilled with steam was determined by the usual diazotization; these amines were identified qualitatively by conversion to the benzoyl derivatives. The first drops of nitrite gave the diazo solution a violet – red color, indicating the presence of traces of o-semidine, volatile in steam. The benzene-ether solution was again cooled with ice and shaken vigorously for 10-15 minutes with 12-15% hydrochloric acid (5-8 ml), diluted with water to dissolve the precipitate formed and the total amount of rearrangement products determined by diazotization. The azo-compound remained in the benzene-ether solution; evaporation of the solvent showed that this material was almost pure. In the experiments with the three isomeric dichlorohydrazobenzenes, the corresponding dichloroanilines were extracted with a 4-5% solution of hydrochloric acid; the rearrangement products were extracted with 30% hydrochloric acid. In the experiment with 2,2'-dichlorohydrazobenzene, the small amounts of azo compound formed were determined colorimetrically [7]. The greater parts of the azo compounds, which are difficultly soluble in organic solvents (4,4'-dichloroazobenzene, 2,2'-dimethoxyazobenzene and, partially, 4,4'-dimethylazobenzene), were conveniently separated from the reaction mixtures directly; the crystals of azo compound separated were carefully washed with very dilute hydrochloric acid. In Experiment 21 with 2,2'-dimethoxyhydrazobenzene, the hydrazo compound was absent from the reaction products – instead of it, the amount of rearrangement products is given in Table 1.

## LITERATURE CITED


[1] L. G. Krolik and V. O. Lukashevich, Proc. Acad. Sci. USSR, 65, No. 1, 37 (1949).

[2] L. G. Krolik and V. O. Lukashevich, Proc. Acad. Sci. USSR, 93, No. 4, 663 (1953).

[3] F. K. Beilstein, Handb. d. Organ. Chem. 9, II Ergzb. 79.

[4] F. K. Beilstein, Handb. d. Organ. Chem. 2, I. Ergzb. 44.

[5] F. K. Beilstein, Handb. d. Organ. Chem. 2, II, Ergzb. 239.

[6] A. Calm and K. Heumann, Ber. 13, 1181 (1880).

[7] V. O. Lukashevich, J. Gen. Chem. 5, 103 (1935).



K. E. Voroshilov Research Institute of
Organic Intermediates and Dyes



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# INVESTIGATION OF THE EFFECT OF THE SOLVENT ON THE POSITION OF THE TAUTOMERIC EQUILIBRIUM IN THE ARYLTHIOCARBAZONE SERIES

P. S. Pel'kis and R. G. Dubenko

(Presented by Academician B. A. Kazanskii, December 27, 1957)

The effect of a solvent on the position of a tautomeric equilibrium is generally known. However, many theoretical questions on this phenomenon have remained unanswered up to the present day. In the last few years M. I. Kabachnik et al., have done much work in this direction [1-6].

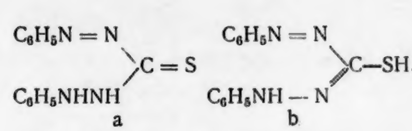
These problems have been examined in a general way by A. N. Nesmeianov and M. I. Kabachnik [7-10].

M. I. Kabachnik [1] applied the modern theory of acid-base equilibrium developed by Brönsted [11] and N. A. Izmailov [12], to the calculation of tautomeric equilibrium. Kabachnik put forward a formula expressing the relation between the constants of the tautomeric equilibrium in two solvents: $S_1$ and $S_2$.

$$pK_{TS_2} = pK_{TS_1} + \text{const.} \tag{1}$$

If the values of $pK_{TS}$ in the two solvents are plotted along coordinate axes, then the points on the graph for all the keto-enols must lie on a line with a slope equal to 1. Checking this showed that the equation put forward was correct for many keto-enols [10]. Recently, M. I. Kabachnik et al., [1] showed that the equation applied to tautomeric equilibria in the dialkylthiophosphate series [6]. It seemed interesting to test whether equation (1) would apply to tautomeric equilibria in the arylthiocarbazone series.

One of us [13] showed that 1,5-diphenylthiocarbazone (dithizone) in solvents was a mixture of thione (a) and thiol (b) tautomers:



The ratio of the thione and thiol forms in the tautomeric mixture depends on the nature of the solvent and the substituent in the aromatic nuclei of the thiocarbazone. It was shown that the short wavelength maximum ($\lambda_{max\,1}$) of the absorption spectrum curve at 450 mμ belonged to the thiol form and the absorption maximum at 620 mμ ($\lambda_{max\,2}$) to the thione form a dithizone. Thus, the maximum in the short wavelength region on the absorption curves of substituted 1,5-diphenylthiocarbazones belong to the thiol forms and the maxima in the long wavelength region – to the thione forms.

From the equation $d_{\lambda\, max\, 1} = l\, c_1\epsilon_1$ and $d_{\lambda\, max\, 2} = l\, c_2\epsilon_2$ it follows that the ratio $\frac{d_{\lambda\, max\, 2}}{d_{\lambda\, max\, 1}} = \frac{c_2\epsilon_2}{c_1\epsilon_1}$ and hence the tautomeric equilibrium constant

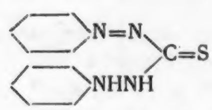
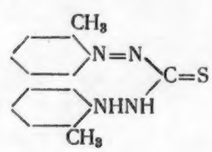
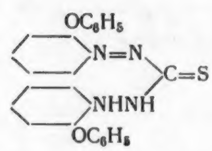
$$K_T = \frac{c_2}{c_1} = \frac{d_{\lambda}\max_2}{d_{\lambda}\max_1}\cdot\frac{\varepsilon_1}{\varepsilon_2}$$

$$pK_T = \lg\frac{d_{\lambda}\max_2}{d_{\lambda}\max_1} + \lg\frac{\varepsilon_1}{\varepsilon_2}\ ; \qquad (2)$$

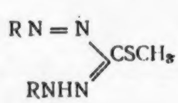
where $d_{\lambda\ max\ 2}$ and $d_{\lambda\ max\ 1}$ are the optical densities (extinctions), c is the concentration, $\epsilon_1$ and $\epsilon_2$ are the molar extinction coefficients of thiol and thione, respectively, and $l$ is the layer thickness.

As the experimental data show, the tautomeric equilibrium constant of dithizone and its substituents in solvents is approximately equal to the ratio $\frac{d_{\lambda\ max\ 2}}{d_{\lambda\ max\ 1}}$. The ratio $\frac{\epsilon_1}{\epsilon_2}$ is practically independent of the solvent and is approximately equal to unity and, therefore, the value of the second term in Equation (2) may be neglected.

TABLE 1

| Thiocarbazone | Benzene | | | Carbon tetrachloride | | | Chloroform | | | Hexane | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\varepsilon_1\cdot10^{-4}$ | $\varepsilon_2\cdot10^{-4}$ | $\varepsilon_1/\varepsilon_2$ | $\varepsilon_1\cdot10^{-4}$ | $\varepsilon_2\cdot10^{-4}$ | $\varepsilon_1/\varepsilon_2$ | $\varepsilon_1\cdot10^{-4}$ | $\varepsilon_2\cdot10^{-4}$ | $\varepsilon_1/\varepsilon_2$ | $\varepsilon_1\cdot10^{-4}$ | $\varepsilon_2\cdot10^{-4}$ | $\varepsilon_1/\varepsilon_2$ |
|  | 11.92 | 11.93 | 1.0 | 12.0 | 11.9 | 1.0 | 12.2 | 12.7 | 0.96 | 8.6 | 8.6 | 1.0 |
|  | 23.33 | 22.6 | 1.03 | 20.8 | 20.6 | 1.01 | 28.8 | 28.8 | 1.0 | 13.56 | 13.76 | 0.99 |
|  | 22.8 | 23.2 | 0.98 | 21.58 | 21.74 | 0.99 | 27.6 | 27.3 | 1.01 | 11.0 | 10.8 | 1.02 |

In order to calculate the molar extinction coefficients, $\epsilon_1$, we took as 100% for the thiol form of the thiocarbazone the absorption intensity at the maxima of the corresponding S-methyl derivatives of dithizone

of the general formula  , that we had synthesized [16]. $\epsilon_2$ was calculated by the

formula $\epsilon_2 = \frac{d_{\lambda\ max\ 2}}{l\,(a - a_1)}$ , where a is the concentration of the appropriate thiocarbazone in mole/liter and $a_1$ is the concentration of the thiol form in the sample (a).

Table 1 gives data on the determination of the tautomeric equilibrium constants of three thiocarbazones

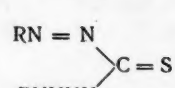
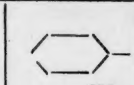
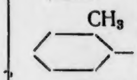
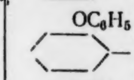
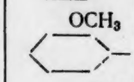
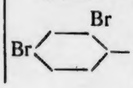
in various solvents. For the thiocarbazones investigated  , Table 2 gives the absorption maxima $\lambda_{max\ 1}$, and $\lambda_{max\ 2}$, the corresponding optical densities $d_{\lambda\ max\ 1}$, $d_{\lambda\ max\ 2}$ and their ratio $\frac{d_{\lambda\ max\ 2}}{d_{\lambda\ max\ 1}} = K_T$.

TABLE 2

| Sample No. | R | Sample No. | Benzene | | | Carbon tetrachloride | | | Chloroform | | | Hexane | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | a | b | $K_T$ | a | b | $K_T$ | a | b | $K_T$ | a | b | $K_T$ |
| 1 |  | (13) | 450/1.6 | 620/2.8 | 1.75 | 450/1.80 | 620/2.81 | 1.56 | 450/1.52 | 610/3.85 | 2.53 | 450/2.8 | 620/2.86 | 1.02 |
| 2 |  | (14) | 470/0.59 | 630/1.51 | 2.56 | 470/1.2 | 630/2.7 | 2.25 | 450/1.24 | 620/4.34 | 3.5 | 450/0.552 | 630/0.888 | 1.61 |
| 3 |  | (13) | 480/1.0 | 650/2.34 | 2.34 | 470/1.056 | 640/2.1 | 1.99 | — | — | — | 470/0.54 | 650/0.79 | 1.46 |
| 4 |  | (13) | 486/1.02 | 659/2.38 | 2.33 | 470/1.06 | 640/2.6 | 2.45 | 470/1.14 | 620/3.35 | 2.94 | 440/0.32 | 630/0.44 | 1.38 |
| 5 |  | (17) | 445/1.30 | 645/1.29 | 0.99 | 450/0.678 | 640/0.55 | 0.81 | 450/0.536 | 630/0.745 | 1.39 | 440/1.23 | 630/0.725 | 0.59 |

Note: a) above the line $\lambda_{max_1}$, below the line $d_{\lambda max_1}$, b) above the line $\lambda_{max_2}$ below the line $d_{\lambda max_2}$.

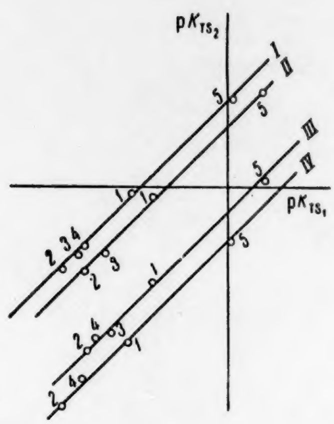



Fig. 1. The relation between $pK_{TS_2}$ and $pK_{TS_1}$ for five thiocarbazones. 1) 1,5-di-(phenyl)-thiocarbazone, 2) 1,5-di-(o-tolyl)-thiocarbazone, 3) 1,5-di-(o-phenoxyphenyl)-thiocarbazone, 4) 1,5-di-(o-methoxyphenyl)-thiocarbazone, 5) 1,5-di-(2,4-dibromophenyl)-thiocarbazone. I) $S_1$ = benzene, $S_2$ = hexane; II) $S_1$ = carbon tetrachloride, $S_2$ = hexane; III) $S_1$ = carbon tetrachloride, $S_2$ = benzene; IV) $S_1$ = benzene, $S_2$ = chloroform.

As the data in Table 2 and Fig. show, the linear character of the relation and the 45° slope of the lines are maintained quite well.

Therefore, we may consider that the equation, put forward by M. I. Kabachnik, extending the rules of the acid-base protolytic equilibrium to cover tautomeric keto-enol equilibrium, is fully confirmed in the arylthiocarbazone series for thione-thiol tautomeric equilibrium.

The arylthiocarbazones (preparations Nos. 1-4) were synthesized by the formazyl method according to the literature data [14, 15]. The absorption spectra of the thiocarbazones and their S-methyl derivatives were measured in suitable solvents at a concentration of $6.6 \cdot 10^{-5}$ mole/liter on an SF-4 spectrometer.

## LITERATURE CITED


[1] M. I. Kabachnik, Proc. Acad. Sci. USSR, 83, 407 (1952).

[2] M. I. Kabachnik, Proc. Acad. Sci. USSR, 83, 859 (1952).

[3] M. I. Kabachnik, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 98.*

[4] M. I. Kabachnik and T. A. Mastriukova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, 163.*

[5] M. I. Kabachnik and S. T. Ioffe, Proc. Acad. Sci. USSR, 91, 833 (1953).

[6] M. I. Kabachnik, S. T. Ioffe and T. A. Mastriukova, J. Gen. Chem. No. 2 (1955).*

[7] M. I. Kabachnik, Prog. Chem. 25, 137 (1956).*

[8] A. N. Nesmeianov and M. I. Kabachnik, Coll. Problems of Chemical Kinetics, Catalysis and Reactivity, Acad. Sci. USSR Press, 1955, pp. 644-698.**

[9] A. N. Nesmeianov and M. I. Kabachnik, J. Gen. Chem. 25, 41 (1955).*

[10] M. I. Kabachnik, Coll. Problems on the Mechanism of Organic Reactions, Kiev, 1954, pp. 126-156.**

[11] J. N. Brönsted, Z. phys. Chem. A, 169, 32 (1934).

[12] N. A. Izmailov, J. Phys. Chem. 24, 321 (1950).

[13] P. S. Pel'kis, Proc. Acad. Sci. USSR, 88, 999 (1953).

[14] D. S. Tarbell, et al., J. Am. Chem. Soc. 70, 1385 (1948).

[15] P. S. Pel'kis and L. S. Pupko, Ukr. Chem. J. 17, 93 (1951).

[16] P. S. Pel'kis and R. G. Dubenko, Proc. Acad. Sci. 110, 798 (1956);* P. S. Pel'kis, R. G. Dubenko and L. S. Pupko, J. Gen. Chem. 27, 2134 (1957).*



Institute of Organic Chemistry
Academy of Sciences USSR



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THE ACID-CATALYZED SYNTHESIS OF ESTERS AND OTHER DERIVATIVES OF CARBOXYLIC ACIDS FROM CARBON MONOXIDE, OLEFINS AND ACYLATING COMPOUNDS

Ia. T. Eidus, K. V. Puzitskii and K. G. Riabova

(Presented by Academician B. A. Kazanskii, January 27, 1958)

The formation of carboxylic esters from carbon monoxide, olefins and alcohols has been studied very little. Up to now, these reactions, which proceed in the presence of acid catalysts, were carried out with all the starting components simultaneously in the reaction mixture and under very drastic conditions (high pressures and temperatures). Thus, mixtures of carbon monoxide, ethyl alcohol vapor and ethylene or propylene gave [1] low yields of ethyl propionate or butyrate at temperatures above 300° and pressures up to 700 atm in the presence of phosphoric acid on charcoal. A mixture of ethylene, propylene and CO at 110° and 500 atm in the presence of boron trifluoride hydrate gave [2] a 14% yield of ethyl $\alpha,\alpha$-dimethylbutyrate. Ethyl $\alpha$-ethyl-$\alpha$-methylbutyrate was formed [3] from CO and $C_2H_4$ at 115° and 1000 atm with boron trifluoride hydrate as the catalyst.

In this work we give the experimental data on a new method of synthesizing esters of carboxylic acids from CO, olefins and alcohols, which proceeds under very mild conditions for this type of reaction (temperatures of 0-50° and pressures from atmospheric to 80 atm). We also examine the possibility of synthesizing other carboxylic acid derivatives under similar conditions.

We synthesized the esters in two stages. At first only the olefins and CO were in the reaction mixture and they reacted with the catalyst (concentrated sulfuric acid) to form an intermediate complex. Then alcohol was added and this reacted with the complex to form the carboxylic esters with the regeneration of the sulfuric acid.

A theoretical consideration of the nature of the intermediate product, formed from CO, olefin and mineral acid resulted in the following conclusions. First, the complex has the character of an acylating agent as is shown by the formation of carboxylic esters when it is treated with an alcohol. Secondly, the complex is very similar in composition and structure and is possibly identical to a mixed anhydride of the sulfuric and the carboxylic acids [4] as is shown by the participation of sulfuric acid in its formation and the elimination of the acid when the complex is treated with alcohol. Finally, the formation of the complex involves the intermediate formation of carbonium ions. This is indicated by the isomeric conversions, which result in esters corresponding to skeletal isomers of the olefin in addition to those corresponding to the original olefin.

All these conclusions, based on experimental facts, make it possible to represent the complex formation by the following reactions [5]:

$$R_1R_2C = CR_3R_4 + H_2SO_4 \rightarrow R_1R_2HC - \overset{+}{C}R_3R_4 + \overset{-}{O}SO_3H \xrightarrow{CO}$$

$$\rightarrow \underset{II}{R_1R_2HC - R_3R_4C - \overset{+}{C}O} + \overset{-}{O}SO_3H \rightleftarrows \underset{III}{R_1R_2HC} - R_3R_4C - \underset{\underset{O}{\|}}{C} - OSO_3H \qquad (1)$$

The last stage — the reaction of the alcohol with the complex (in form II or III) — may be expressed by the reaction:

$$\text{II (or III)} + HX \rightarrow H_2SO_4 + \underset{\text{IV}}{R_1R_2HC - R_3R_4C - \underset{\overset{\|}{O}}{C}X} \qquad (2)$$

where x is the alkoxyl group.

Isomeric conversions of the carbonium ions I or II should give esters, isomeric with ester IV.

The acylating properties of the complex, resulting from the electrophilic nature of the carbonium ion II or from the anhydride nature of form III, are of a general character. They should then appear in reaction with other compounds, HX, which contain active hydrogen. Therefore, equation (2) expresses a series of reactions which give carboxylic acid derivatives. When X = $H_2N-$, $HNR-$, $R_2N-$, $Cl-$, $Br-$, $RCOO-$ etc. equation (2) represents the formation reactions of amides, acid halides, anhydrides etc, respectively. In the particular case when X = $HO-$, this represents the synthessi of carboxylic acids carried out by Koch [6] under conditions analogous to those described above.

In this paper we describe briefly the results obtained in investigating the formation of methyl esters of carboxylic acids (i.e., when X = $CH_3O-$) from isobutylene and from liquid olefins.

The reaction with isobutylene was carried out at 0° and atmospheric pressure in a cylindrical glass vessel containing 0.5 liters of 96% sulfuric acid. With vigorous stirring, 237 liters of a gas mixture with the composition 1 $i\text{-}C_4H_8$ : 1 CO was passed through the acid; 19.4 liters (16.6%) of CO and 118 liters (100%) of $i\text{-}C_4H_8$ were absorbed. After separation from the oily isobutylene polymer, the lower acid layer was treated with 0.7 liters of methyl alcohol. Then the reaction mixture was diluted with 2 liters of water and we isolated 73 ml of methyl esters of carboxylic acids with a boiling range 80.0-197.5°; the yield was 65.7 and 10.8% on the CO and the isobutylene used in the reaction, respectively. Fractionation on a column with an efficiency of 40 t.p. gave methyl esters of saturated monobasic carboxylic acids: $C_5$ 21% and $C_6$ 3%.

For comparison, carboxylic acids were prepared from isobutylene and CO, under analogous conditions, using Koch's method [6] of treating the acidic complex with water and this gave a yield of 47.8 and 14.9% on the CO and isobutylene reacted, respectively. Treatment with diazomethane converted the acids to the methyl esters, which boiled in the range 88.5-220°. Fractionation on the same column gave esters of $C_5$ (38%) and $C_6$ (4%) acids.

For liquid olefins we used a fraction with b.p. 32-124°, the hydrocondensation product of CO and propylene [7], which had $d_4^{20}$ 0.6775, $n_D^{20}$ 1.3902, bromine number 99.7 and 61.2 % olefin content. The reaction was carried out in a stainless steel autoclave, loaded with 0.5 liter of 96% sulfuric acid and up to 80 atm of CO. 215 ml of the above fraction was added over a period of 6 hours with vigorous stirring. 16.5 liters of CO were consumed. The reaction mixture contained paraffinic hydrocarbons in the upper layer, which were from the initial fraction, and the acid complex (see Equation (1)) and excess sulfuric acid were in the lower layer. 0.7 liter of methyl alcohol was added to the lower layer and the reaction mixture diluted with 2 liters of water. We separated 101 ml of a mixture of carboxylic acid methyl esters with a boiling range 28-130° at 2 mm Hg; the yield was 63% on the initial olefin and 78% on the CO reacted. Fractionation on the above column gave methyl esters of saturated carboxylic acids: $C_5$ 12%, $C_6$ 28%, $C_7$ 27% and $C_8$ 6%.

## LITERATURE CITED


[1] W. E. Vail, U. S. Pat. 1979717 (1934); Canad. Pat. 342957 (1934); Chem. Abstr. 29, 181 (1935); 28, 6444 (1934).

[2] T. A. Ford, U. S. Pat. 2424653 (1947); Chem. Abstr. 41, 6576 (1947).

[3] J. R. Roland, J. D. C. Wilson and W. E. Hanford, J. Am. Chem. Soc. 72, 2122 (1950).

[4] H. Meyer, Monatsh. f. Chem. 24, 840 (1904).

[5] M. Orchin and I. Wender, Catalysis, 5,8 (1957).

[6] H. Koch. Brennst.-Chem. 36, 321 (1955).

[7] Ia. T. Eidus, K. V. Puzitskii and N. I. Ershov, Trans. All-Soviet Conf. on Compl. Chem. Processing of Petroleum Gases, Acad. Sci. USSR Press, 1956, p. 616.

N. D. Zelinsky Institute of Organic Chemistry
Academy of Sciences USSR

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# ELECTRONOGRAPHIC INVESTIGATION OF THE POLYMORPHISM OF ZIRCONIUM DIOXIDE IN THIN FILMS

I. I. Korobkov and D. V. Ignatov

(Presented by Academician I. P. Bardin, January 21, 1958)

A study of the polymorphism of zirconium dioxide in thin films has been carried out for the first time and was brought about, on one hand, by the contradictory results obtained by different investigators studying polymorphism in massive samples of monoclinic $ZrO_2$, and on the other hand, by the obscurity of the problem of the structure of the oxide film developing on zirconium by corrosion in oxidizing media.

A detailed review of the four possible modifications (monoclinic, tetragonal, cubic, and rhombohedral) of $ZrO_2$, with a description of their formation and range of occurrence, is given in the monograph by Lustman [1]. According to x-ray data presented in this review, the lattice of the monoclinic modification of $ZrO_2$ is a distorted cubic lattice of the $CaF_2$ type with parameters (in A): $a = 5.17_4$; $b = 5.26_6$; $c = 5.30_8$; $\beta = 80°48'$. This modification is stable up to 1000°.

Above 1000° the tetragonal modification of $ZrO_2$ is stable; the parameters of its lattice (in A) are: $a = 5.07$ and $c = 5.16$.

The cubic modification of $ZrO_2$ is secured at room temperature by chilling from 2000° in the presence of added MgO; it has a fluorite structure with the parameter $a = 5.098$ A. It is considered stable above 1900°.

After prolonged heating of monoclinic zirconium dioxide at 1900°C, the rhombohedral form of $ZrO_2$ is produced. It is represented in the same way as a pseudohexagonal form with $a = 3.598$ A and $c/a = 1.633$.

However, from a number of investigations [2-5] it appears that two forms of zirconium dioxide indisputably exist: the monoclinic and the tetragonal, which pass over reversibly from the one to the other at temperatures of 1000-1100°. Baked or fused monoclinic zirconium dioxide contaminated with hafnium dioxide (less than 2%) served as the starting material for the study of polymorphism in the work of the authors indicated. Domogala and Macpherson [6] studied the polymorphism of $ZrO_2$ by the x-ray method on samples of fused zirconium dioxide practically free of hafnium dioxide. Using heat treatment of the samples at temperatures of 900, 1210, 1745, and 2315° with subsequent chilling, these authors attempted to secure the possible modifications of $ZrO_2$. The authors note that in all cases only the unchanged monoclinic modification was found.

On the surface of zirconium oxidized in different media (in oxygen, in air, or steam) under fixed conditions and at temperatures from 20 to 800° oxide films were found [1] that consisted of the oxide $ZrO_2$ with the structure of one of 3 modifications: monoclinic, tetragonal, or cubic. These data do not agree with the results of the investigation of the above-mentioned authors [2-5], according to which only the monoclinic phase of $ZrO_2$ exists below 1000°.

Methods. The investigation of the polymorphism of zirconium dioxide was carried out on samples in the form of thin films of zirconium (thickness 400-600 A) by an electronographic method. Use of a special apparatus for heating the sample (up to 1100°) directly in the electronograph permitted observation of the structural transformations of the zirconium dioxide with relation to temperature and time of heating, without cooling the sample.

This apparatus consisted of two strips of zirconium 0.2 mm thick, each having a hole 0.8 mm in diameter; the sample was placed between the strips, opposite the hole. These strips were heated with direct current; the sample, which was in thermal equilibrium with the apparatus, was heated along with them. The bulb of a platinum-platinorhodium thermocouple was pressed tightly to the zirconium films by means of a pressure clamp. While the electronogram was exposed for 0.5 sec., the current was turned off, since the magnetic field created by it distorted the diffraction picture. From experiments on the heating and cooling of samples in the same electronograph, it was established that cooling from a high temperature to room temperature does not bring about a change in the structure of zirconium dioxide characteristic of each heating temperature; therefore, electronograms were further obtained only from samples cooled to room temperature. Thin films of zirconium prepared by vaporization and condensation in vacuo of doubly refined zirconium iodide of 99.9% purity served as the starting samples. NaCl crystals in the form of a film were used as a base on which the metal was condensed. To prepare thin layers of zirconium, a glass high-vacuum apparatus was made which permitted attaining a vacuum of $\sim 10^{-7}$ mm Hg; such a vacuum was obtained by using a zirconium gas absorber. A horizontal spiral 2 mm in diameter and 10 mm long of tungsten wire 0.2 mm in diameter served as the vaporizer. The spiral was previously tempered in a high vacuum. After this, a rod of zirconium 0.2 mm in diameter was placed inside the spiral. When a vacuum of $10^{-7}$ mm Hg was reached, a current of 5-7 amp was passed through the spiral until the zirconium rod started to melt.

When the zirconium melted, droplets were formed on several coils of the spiral, from which the zirconium vigorously vaporized. The thickness of the films was limited by the time of vaporization and the distance of the foundation from the vaporizer.

The zirconium crystallized on the cold foundation in the metallic state, as indicated by the very diffuse diffraction lines in the electronograms (see electronogram in Fig. 1). Therefore we adopted the practice of heating the foundation to a temperature of 200-250°. The heater was made from a strip of zirconium foil 0.05 mm thick, through which the current was passed.

The experiments showed that the vaporization of zirconium must be conducted with great care, with particular attention to the vacuum in the system, since the zirconium on melting reacts actively with the residual gas, and if the vacuum is not sufficient ($10^{-5}$ mm Hg), the films obtained are partially oxidized. Therefore it was necessary before vaporization carefully to degas the foundation, which we did by heating it to 600° for 1 hour. The admission of air into the system after obtaining the films was carried out over some period of time after disconnecting the pumps, which guaranteed gradual passivation of the zirconium film by the residual oxygen and protected it from deep-seated oxidation on admission of the air.

The film was peeled from the NaCl foundation by gradual immersion in distilled water. The exfoliated film was then washed free of NaCl in several baths with distilled water. The pieces of zirconium film floating on the surface of the water were drawn out onto zirconium strips and onto platinum frames with a hole 0.8 mm in diameter. Then these thin zirconium films were heated in pure oxygen at 270°, where, as had been established previously, appreciable oxidation of zirconium starts, i.e., at this temperature the lines of the metal in the electronograms disappear and the lines of the oxide appear.

The electronographic studies were carried out in an electronograph of the construction of the Institute of Metallurgy of the Academy of Sciences USSR. Its dispersion capacity was 0.005 A per 0.2 mm for a diffraction distance of 500 mm.

A constant electronograph of $2\lambda L$ was determined in each case from electronograms of a standard sample, a thin film of aluminum.

The samples were heated in air (in an ordinary electric muffle furnace), in oxygen, and in a vacuum (in a special apparatus and in the electronograph itself) at temperatures from 275 to 1300° with intervals of 25°. The temperature was determined with a thermocouple with an accuracy of ±10°.

Results of the investigation are presented in the form of electronograms in Fig. 2 and in the corresponding tables of calculations (Tables 1 and 2).

From the electronogram 2a, obtained from a thin layer of zirconium, and the corresponding Table 1, it is seen that the values of the interplanar distances of the crystal lattices of this layer correspond to $\alpha$-zirconium, but in comparison with the x-ray data they are increased by 2-3%. The intensities of the lines agree with the

intensities determined from x-ray studies. The increase in the lattice distance, apparently, is connected with solution of oxygen in the zirconium film. The electronogram in Fig. 2a is characteristic of thin zirconium films obtained on preheated foundations.

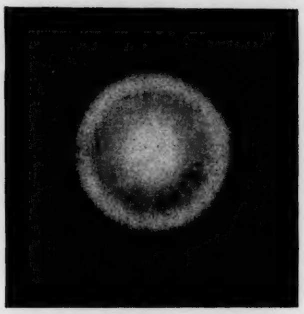

Fig. 1. Electronogram of a thin layer of Zr condensed on a cold base (18°).

Analysis of the electronogram (Fig. 2b and Table 2) from a film of zirconium heated at 300° shows that this film was completely oxidized, and the diffraction picture corresponds to the cubic modification of zirconium oxide $ZrO_2$ (with the presence of one odd line d = 2.10 A). The value for the lattice distance of this modification was found to be a = 5.10 A, which agrees well with the value for this measurement determined by the x-ray method [1]. The somewhat increased width of the diffraction lines in the electronograms of Figs. 2a and 2b indicate that both $\alpha$-Zr and $ZrO_2$ in this instance were fine-grained.

On heating from 300 to 600° the interference rings in the electronograms from the zirconium dioxide film become more and more sharp and conform with the cubic modification mentioned, and beginning with 650° a splitting of some rings is found (for example, the ring of plane (002)) for cubic $ZrO_2$, which indicates the appearance in the layer of a new modification of $ZrO_2$. Calculation of the electronogram from it shows that it has a tetragonal lattice, the interplanar distances of which, as seen from Table 2, agree with their x-ray values. The characteristic electronogram obtained at 700°, in which the divided rings can be seen, is given in Fig. 2c.

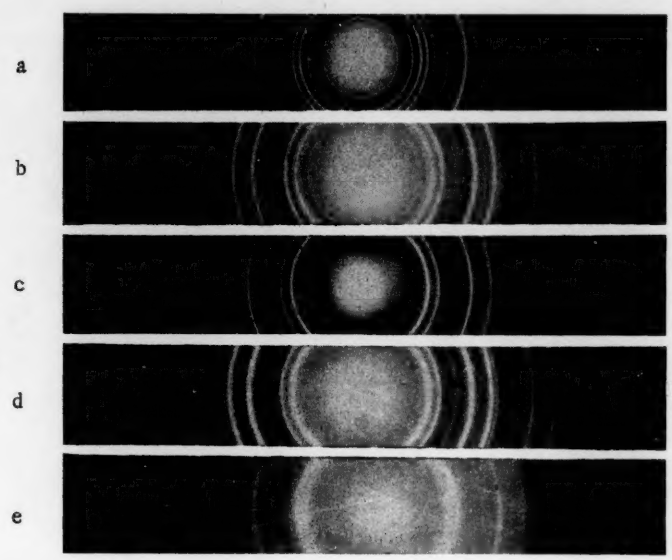

Fig. 2. Electronograms of a thin layer of zirconium heated at different temperatures in oxygen; a) 18°; b) 300°; c) 700°; d) 850°; e) 1000°.

TABLE 1

Results of Calculation of Electronogram from Thin Layer of α-Zr, Obtained by Vaporization in Vacuo ($10^{-6}$ mm Hg)

| Ring No. | Diameter of ring, mm* | Intensity of ring | d/n expt. | d/n x-ray | Ring No. | Diameter of ring, mm | Intensity of ring | d/n expt. | d/n x-ray |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 21.3 | s. | 2.85 | 2.78 | 7 | 40.95 | w. | 1.48 | 1.46 |
| 2 | 23.0 | m. | 2.64 | 2.56 | 8 | 43.1 | w. | 1.41 | 1.36 |
| 3 | 24.4 | v.s. | 2.49 | 2.44 | 9 | 44.3 | m. | 1.37 | 1.34 |
| 4 | 31.5 | w. | 1.92 | 1.88 | 10 | 48 | v.w. | 1.26 | 1.22 |
| 5 | 34.0 | v.w. | 1.78 | — | 11 | 57.8 | m. | 1.05 | 1.038 |
| 6 | 37 | s. | 1.64 | 1.61 | 12 | 61.4 | w. | 0.99 | 0.97 |

*Notes: Here and in Table 2: s – strong, m – medium, w – weak, v.s. – very strong, etc.

In this instance it is difficult to speak of the simultaneous existence of two forms of $ZrO_2$ – cubic and tetragonal – since their parameters are very close, but apparently the process of transition from the cubic to the tetragonal form goes by stages, as indicated by some electronograms obtained from the layer at 500° in which a splitting of the line from the planes with corresponding indexes is noted. In the temperature interval from 750 to 800°, along with the lines of the tetragonal modification of $ZrO_2$, there appear in the electronograms the lines of the monoclinic modification of the oxide, which become more intense with an increase in the temperature of heating, while the lines of the tetragonal modification gradually disappear, and at 1100° purely the monoclinic modification of the oxide $ZrO_2$ is observed, the interplanar distances of which agree with the tabular data (see Fig. 2b and Table 2). This monoclinic modification of zirconium dioxide is maintained on heating up to 1300°.

TABLE 2

Interplanar Distances and Relative Intensities of Lines in Electronograms Obtained from $ZrO_2$ in Relation to Heating Temperature

| 300° | | | 700° | | | 850° | | | 1000° | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Intensity of ring | $d_{expt.}$, A | $d_{x\text{-}ray}$, A | Intensity of ring | $d_{expt.}$, A | $d_{x\text{-}ray}$, A | Intensity of ring | $d_{expt.}$, A | $d_{x\text{-}ray}$, A | Intensity of ring | $d_{expt.}$, A | $d_{x\text{-}ray}$, A |
| v.s. | 2.94 | 2.94 | v.s. | 2.94 | 2.94 | w. | 5.12 | 5.10 | m. | 5.16 | 5.10 |
| m. | 2.54 | 2.54 | m. | 2.59 | 2.57 | m. | 3.67 | 3.69 | m. | 3.69 | 3.69 |
| w. | 2.10 | — | m. | 2.53 | 2.53 | m. | 3.16 | 3.19 | v.s. | 3.17 | 3.19 |
| s. | 1.80 | 1.80 | w. | 2.09 | — | v.s. | 2.94 | 2.94 | s. | 2.86 | 2.85 |
| m. | 1.54 | 1.53 | s. | 1.80 | 1.80 | m. | 2.83 | 2.85 | m. | 2.63 | 2.63 |
| w. | 1.46 | 1.47 | m. | 1.55 | 1.55 | w. | 2.57 | 2.58 | m. | 2.55 | 2.55 |
| w. | 1.27 | 1.27 | m. | 1.52 | 1.52 | w. | 2.53 | 2.53 | w. | 2.34 | 2.34 |
| m. | 1.17 | 1.17 | w. | 1.47 | 1.47 | w. | 2.31 | 2.34 | w. | 2.29 | — |
| v.w. | 1.15 | 1.14 | w. | 1.35 | — | w. | 2.19 | 2.21 | m. | 2.22 | 2.21 |
| m. | 1.04 | 1.04 | v.w. | 1.29 | 1.29 | w. | 2.02 | 2.01 | w. | 2.01 | 2.01 |
| w. | 0.98 | 0.98 | m. | 1.26 | 1.26 | s. | 1.80 | 1.80 | m. | 1.85 | 1.85 |
| | | | | | | w. | 1.70 | 1.70 | w. | 1.80 | 1.81 |
| | | | m. | 1.175 | 1.165 | w. | 1.65 | 1.65 | | | |
| | | | | | | m. | 1.55 | 1.55 | | | |
| | | | | | | s. | 1.52 | 1.52 | | | |
| Cubic | | | Tetragonal | | | Tetragonal + monoclinic | | | Monoclinic | | |

Thus, by oxidation of a thin layer of zirconium at 270° the cubic modification of $ZrO_2$ is formed, which upon heating undergoes a polymorphous conversion of the monotropic type: the cubic lattice is stretched along one axis and becomes tetragonal; then with an increase in temperature of heating (700-1100°) it is distorted still more and converted to a monoclinic lattice.

As is indicated above, the polymorphism was studied by heating a thin film of cubic $ZrO_2$ in a vacuum, oxygen, or air. In all these instances identical, regular transitions of the cubic modification to the tetragonal were found, and of the latter to the monoclinic, in the same temperature intervals. The results obtained therefore permit the statement that the polymorphic conversions discovered are characteristic of zirconium dioxide and are not a consequence of the solution of oxygen in $ZrO_2$, or of the attainment by the oxide $ZrO_2$ of an exact stoichiometric composition; in this instance the nitrogen of the air also does not play a part. In conclusion, it should be noted that our data and the results reported by Domogala and MacPherson permit consideration of monoclinic $ZrO_2$ as the stable form of zirconium oxide, which is the final conversion product of $ZrO_2$ in the temperature range 300-1300°.

## LITERATURE CITED


[1] B. Lustman, The Metallurgy of Zirconium, USA, 1955.

[2] I. Pierrey, Ann. Chem. 4, 135 (1949).

[3] G. Gurties, J. Am. Ceram. Soc. 33, No. 6, 198 (1950).

[4] W. Boldwin, Chem. Eng. Progr. No. 11, 875 (1948).

[5] R. F. Geller and P. Javorsky, J. Res. Nat. Bur. Stand. 35, 189 (1945).

[6] R. F. Domogala, D. MacPherson and M. Hansen, Symposium on Zirconium, Pt. II, IL, 1955, p. 105. *



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# REACTION OF TROPYLIUM SALTS WITH VINYL ETHERS AND WITH β-CHLOROMERCURIACETALDEHYDE

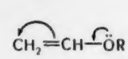
Member-Correspondent of Acad. Sci. USSR D. N. Kursanov, M. E. Vol'pin, and I. S. Akhrem

Characteristic of the stable aromatic cation cycloheptatrienylium (tropylium) is its ability to enter into reactions with nucleophilic reagents. Thus, according to the data of Doering and Knox [1], tropylium salts react readily with $NH_3$, $H_2S$, $OH^-$, amines, and organolithium and organomagnesium compounds.

It might be expected that the electrophilic nature of the tropylium cation would be sufficient for it to react even with more weakly nucleophilic reagents — the vinyl ethers.

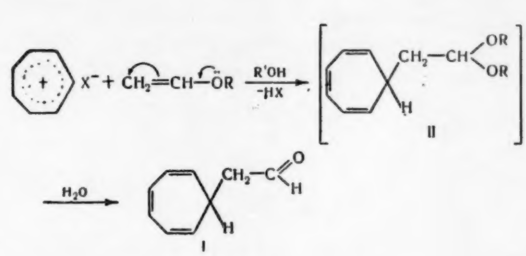
Actually it appears that tropylium salts in aqueous or alcoholic solutions react vigorously even in the cold with the vinyl ethers, with the evolution of heat.

The high reactivity of the vinyl ethers in this reaction is a result of the influence of the electron-donating ether group



Compounds with isolated or conjugated double bonds, but without activating substituents (for example, methylcyclohexene, cycloheptatriene, etc.) or with electron-accepting substituents (cinnamic acid, acrylic acid, acrylonitrile, allyl chloride, etc.) do not react with tropylium salts under the same conditions.

In all cases, regardless of the nature of the anion of the starting tropylium salt (bromide or perchlorate) and of the character of the alkyl group in the vinyl alkyl ethers (vinyl ethyl, vinyl isopropyl, vinyl butyl), one and the same product is obtained — cycloheptatrienylacetaldehyde (I):



(where X = Br or $ClO_4$; R = $C_2H_5$, iso-$C_3H_7$ or $C_4H_9$; R' = H or $C_2H_5$).

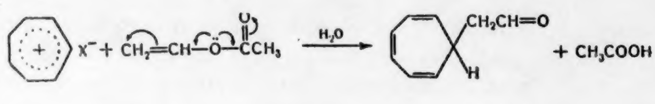
This reaction is similar to the addition of mercury salts to vinyl ethers, discovered by A. N. Nesmeianov and I. F. Lutsenko [2]:

$$HgX_2 + CH_2{=}CHOR \xrightarrow[-HX]{R'OH} \left[XHgCH_2CH\begin{matrix}OR\\ OR'\end{matrix}\right]$$

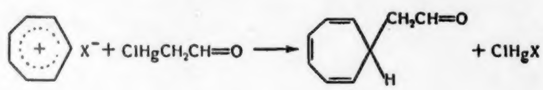
$$\xrightarrow{H_2O} XHgCH_2CH{=}O$$

By analogy with the latter reaction it might be thought that the mechanism of the reaction of tropylium salts with the vinyl ethers includes an attack by the $C_7H_7^+$ ion on the double bond of the vinyl ether with simultaneous (or subsequent) reaction by a molecule of the solvent (water or alcohol). Probably an intermediate reaction product is the acetal or hemiacetal (II).

On going from the vinyl ethers to vinyl acetate the rate of reaction with tropylium salts is markedly decreased, a fact which apparently is connected with the partial drawing away of the electrons of the C = O group.



Cycloheptatrienylacetaldehyde also was obtained by a counter synthesis — by the reaction of the tropylium salts (bromide and perchlorate) with β-chloromercuriacetaldehyde.



As a result of the replacement of the mercury atom by the tropylium group, an aldehyde was produced that was identical with that obtained from the vinyl ethers. This reaction is the first example studied of the reaction of organomercury compounds with tropylium salts.

It is essential to note that the reaction of tropylium salts with β-chloromercuriacetaldehyde proceeds like a C-alkylation. As has been shown by A. N. Nesmeianov and I. F. Lutsenko [3], in exactly the same way triphenylmethyl chloride reacts to yield triphenylmethylacetaldehyde; at the same time, the acyl halides O-acylate β-chloromercuriacetaldehyde.

Cycloheptatrienylacetaldehyde gives characteristic aldehyde reactions, forming a 2,4-dinitrophenylhydrazone and a dimedon derivative. The latter is especially suitable for identification of this aldehyde. The presence of three double bonds in cycloheptatrienylacetaldehyde was demonstrated by its catalytic hydrogenation on platinum black; in this procedure 3 moles of $H_2$ were added and cycloheptylacetaldehyde was formed.

It is interesting to note that cycloheptatrienylacetaldehyde is also produced by the reaction of tropylium salts with acetaldehyde [4].

## EXPERIMENTAL

Reactions of tropylium salts with vinyl ethers. A solution of 1.7 g (0.01 mole) of tropylium bromide in 10 ml of water was shaken for 15-20 minutes with 0.72 g (0.01 mole) of vinyl ethyl ether and was extracted with ether. The ether extracts were washed with water and dried over $MgSO_4$. The ether was distilled off under reduced pressure, and the residue was distilled in vacuo. A fraction was collected with b. p. 63-67°/2 mm; $n_D^{25}$ 1.5310. Yield 0.77 g (58%). After repeated distillation the b. p. of the cycloheptatrienylacetaldehyde was 62°/2 mm, $n_D^{20}$ 1.5314, $d_4^{20}$ 1.0204, $\lambda_{max}$ 260 mμ (log ε 3.63); $\lambda_{min}$ 237 mμ (log ε 3.43), $MR_{calc}$ = 40.17 (without taking into account the exaltation of the conjugated double bonds); $MR_{found}$ = 40.70.

Found %: C 80.79, 80.63; H 7.46, 7.48. $C_9H_{10}O$. Calculated %: C 80.56; H 7.51.

Cycloheptatrienylacetaldehyde gave characteristic aldehyde reactions: it reduced Fehling's solution and ammoniacal silver nitrate solution; it gave a red color with sodium nitroprusside and with benzidine. The 2,4-dinitrophenylhydrazone of cycloheptatrienylacetaldehyde was a yellow powder; it decomposed above 190° (from nitromethane). The dimedon derivative formed colorless needles, m. p. 146.5° (from alcohol). A mixed sample with dimedon melted at 127-128°.

Found %: C 75.90, 75.41; H 8.14, 8.13. $C_{25}H_{32}O_4$. Calculated %: C 75.72; H 8.13.

Under the same conditions there was obtained from 7.8 g (0.041 mole) of tropylium perchlorate in 5 ml of water and 3 g (0.0416 mole) of vinyl ethyl ether 3.24 g of cycloheptatrienylacetaldehyde (yield 59%). Dimedon derivative: m. p. 146°

Similarly there was obtained from 1.9 g (0.01 mole) of tropylium perchlorate and 0.86 g (0.01 mole) of isopropyl vinyl ether 0.59 g of cycloheptatrienylacetaldehyde, yield 44%. Dimedon derivative: m. p. 145-146°.

From 1.7 g (0.01 mole) of tropylium bromide and 0.86 g ( 0.01 mole) of vinyl isopropyl ether there was obtained 0.75 g of cycloheptatrienylacetaldehyde (yield 56%). Dimedon derivative: m. p. 145°.

From 3.42 g (0.02 mole) of tropylium bromide and 2 g (0.02 mole) of vinyl butyl there was obtained 1.58 g of cycloheptatrienylacetaldehyde (yield 59%). Dimedon derivative: m. p. 145-146°.

From 3.42 g (0.02 mole) of tropylium bromide and 1.72 g (0.02 mole) of vinyl acetate in water there was formed in a day 0.48 g of cycloheptatrienylacetaldehyde (yield 17%). Dimedon derivative: m. p. 146°.

In all experiments with vinyl ethers the same aldehyde was formed; mixed samples of the dimedon derivatives from the various experiments gave no depression in melting point.

Reaction of tropylium salts with β-chloromercuriacetaldehyde. 1.9 g (0.01 mole) of tropylium perchlorate and 2.79 ( 0.01 mole) of β-chloromercuriacetaldehyde were shaken in a mixture of 10 ml of benzene and 5 ml of water for 2 days. The precipitate was separated by filtration, and washed many times with benzene. The benzene extracts were dried over $MgSO_4$. The benzene was distilled off under reduced pressure at a temperature no higher than 30°. The residue was distilled in vacuo. 0.54 g of cycloheptatrienylacetaldehyde was obtained ( yield 40%), b. p. 64-66° /2.5 mm, $n_D^{20}$ 1.5314. The dimedon derivative (m. p. 146.5°) gave no depression in melting point when mixed with the dimedon derivative of the aldehyde obtained from vinyl ethyl ether. Similarly, there was obtained from 1.71 g (0.01 mole) of tropylium bromide and 2.79 g (0.01 mole) of β-chloromercuriacetaldehyde in water-benzene mixture (1 : 1) 0.56 g of cycloheptatrienylacetaldehyde (yield 42%). The yield of cycloheptatrienylacetaldehyde was 50% when the same reaction was carried out with continuous agitation of the reaction mixture (water + $CCl_4$) in a current of $N_2$ and with periodic withdrawal of the aldehyde from the reaction mixture.

Hydrogenation of cycloheptatrienylacetaldehyde. 0.4097 g of cycloheptatrienylacetaldehyde was hydrogenated in alcohol over platinum black at 21.5° and 733.2 mm Hg. The hydrogenation was completed in 30 minutes. 225 ml of $H_2$ was absorbed, which corresponds to 94.5% calculated on the basis of 3 double bonds. The catalyst was filtered off, and the alcoholic solution was evaporated in vacuo. The cycloheptylacetaldehyde that was produced was identified as the 2,4-dinitrophenylhydrazone and the dimedon derivative.

2,4-dinitrophenylhydrazone m. p. 98° (from alcohol).

Found %: C 56.30, 56.80; H 6.25, 6.51. $C_{15}H_{20}N_4O_4$. Calculated %: C 56.24; H 6.29.

Dimedon derivative: m. p. 170.5° (from alcohol).

Found %: C 74.58, 74.45; H 9.43, 9.50. $C_{25}H_{38}O_4$. Calculated %: C 74.58; H 9.51.

LITERATURE CITED

[1] W. E. Doering and L. H. Knox, J. Am. Chem. Soc. 76, 3203 (1954); 79, 352 (1956).

[2] A. N. Nesmeianov, I. F. Lutsenko and N. I. Vereshchagina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1947; 63; A. N. Nesmeianov, I. F. Lutsenko and R. M. Khomutov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 942.*

[3] A. N. Nesmeianov and I. F. Lutsenko, Proc. Acad. Sci. USSR, 59, 707 (1948); A. N. Nesmeianov, I. F. Lutsenko and Z. M. Tumanova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1949, 601.

[4] M. E. Vol'pin, I. S. Akhrem and D. N. Kursanov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957,* 1501.

Institute of Organoelementary Compounds of the Academy of Sciences USSR

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# NETWORK STRUCTURE OF VULCANIZATES OF CARBOXYL-CONTAINING POLYMERS

I. Ia. Poddubnyi, E. G. Erenburg and E. I. Starovoitova

(Presented by Academician V. A. Kargin, January 31, 1958)

It is now well known that the basic physico-mechanical properties of rubbers depend essentially on the molecular structure of the starting polymer. At the same time it is certain that a no less important factor in determining these properties is the structure of the vulcanization network—its density, regularity, the stability of the vulcanization bonds, and the like.

Of special interest from the point of view of the investigation of the structure of the vulcanization network are the rubbers prepared on the basis of caoutchoues, the macromoleeules of which contain small amounts of functional groups, for example carboxyl groups [1].

The vulcanization of such carboxyl-containing polymers with oxides of metals leads to the production of highly stability in unadulterated mixtures with a large coefficient of elasticity, characterized, however, by a considerable fluidity [2]. But the latter is easily eliminated by the introduction into the mixture of the usual vulcanizing agents (thiuram, etc.).

Thus, vulcanizates of carboxyl-containing rubbers, differing very little from the usual synthetic rubbers in the molecular structure of the starting polymer, have specific physico-mechanical properties connected, apparently, with peculiarities of the structure of their vulcanization network.

An investigation of the structure of the vulcanization network of polymers of the type indicated was carried out by us by determining the equilibrium swelling of the vulcanizates in organic solvents. The use of this method was based on the statistical theory of three-dimensional polymers of Flory and Rehner [3], which relates the magnitude of equilibrium swelling Q to the average magnitude of the molecular weight of the section of the chain included between the neighboring connections of the network.

According to this theory

$$M_c = -\frac{\rho V_1 v_2^{1/3}}{\mu v_2^2 + v_2 + \ln(1 - v_2)}, \qquad (1)$$

where $\mu$ is a thermodynamic constant characterizing the reaction in the given polymer-solvent system, $\nu_2$ is the volumetric fraction of the polymer upon equilibrium swelling, equal to $\nu_2 = \frac{1}{Q+1}$ (Q is the volume of the solvent absorbed by unit volume of the polymer). $V_1$ is the molar volume of the solvent, $\rho$ is the density of the polymer. (The value $M_c$, obviously, is inversely proportional to the number of cross bonds in the vulcanizate.)

The method used by us when there were two types of bonds present — chemical bonds formed with thiuram and "salt" bonds formed by the carboxyl groups of the polymer with the metal oxides — permitted us not only to determine separately the number of vulcanization connections of both types, but also to reach definite conclusions relative to the nature of the "salt" bonds.

With this objective, the magnitude of the equilibrium swelling was measured for each sample in pure benzene and in benzene with a small admixture (~1%) of glacial acetic acid. Addition of the acetic acid destroyed the "salt" bonds, as was shown by the complete solubility in this case of all the samples that were vulcanized only with metal oxides.

TABLE 1

Network Density of Vulcanizates Prepared in the Presence of Various Metal Oxides (vulcanization 240 min. at 143°)

| Expt. No. | Oxide | Amount of oxide, % | $M_c \cdot 10^{-3}$ | | | Amount of thiuram reacted, % of that introduced | Amount of bound carboxyl groups, % |
|---|---|---|---|---|---|---|---|
| | | | total | thiuram | "salt" | | |
| Hardness of starting rubber 425 g, methacrylic acid content 1.5% | | | | | | | |
| 1 | MgO | 3 | 13.6 | 42 | 20 | 14.5 | 29.0 |
| 2 | MgO | 5 | 14.7 | 41 | 22 | 14.5 | 25.0 |
| 3 | CaO | 3 | 26.0 | 43 | 65 | 14.0 | 9.0 |
| 4 | CaO | 5 | 20.0 | 38 | 42 | 15.5 | 14.0 |
| 5 | ZnO | 10 | 15.3 | 21 | 53 | 28.0 | 11.0 |
| Hardness of rubber 1825 g, methacrylic acid content 1.5% | | | | | | | |
| 6 | MgO | 3 | 9.6 | 25 | 16 | 24.5 | 37.0 |
| 7 | MgO | 5 | 10.0 | 25 | 18 | 24.0 | 33.0 |
| 8 | CaO | 3 | 16.5 | 21 | 75 | 28.0 | 8.0 |
| 9 | CaO | 5 | 13.0 | 21 | 35 | 28.0 | 17.0 |
| 10 | ZnO | 10 | 10.2 | 14 | 40 | 43.5 | 15.0 |
| Hardness of rubber 900 g, methacrylic acid content 0.75% | | | | | | | |
| 11 | MgO | 3 | 16.5 | 23 | 60 | 26.0 | 20.0 |
| 12 | MgO | 5 | 16.5 | 22 | 65 | 27.0 | 18.0 |
| 13 | CaO | 3 | 19.0 | 24 | 107 | 25.0 | 10.0 |
| 14 | CaO | 5 | 16.0 | 21 | 38 | 29.0 | 18.0 |

Thus, while the magnitude of the equilibrium swelling in the pure solvent corresponds to the total number of vulcanization bonds (n), the value of Q in solvent with acetic acid added characterizes the density of only the "thiuram" lattice ($n_T$), and consequently the number of "salt" connections is equal to the difference $n - n_T$.

The indicated method was used to investigate the structure of a number of vulcanizates of divinylstyrene carboxyl-containing rubbers (with a methacrylic acid content of 0.75 and 1.5%), which were vulcanized in the presence of 2% of thiuram and various amounts of Mg, Ca, and Zn oxides.

It was established that the density and structure of the network depends essentially on the nature of the oxide. Thus, the amount of "salt" bonds was greatest for the vulcanizates prepared in the presence of MgO and least with ZnO, when from 8 to 40% of the carboxyl groups* contained in the polymer participated, in all, in the formation of vulcanization bonds (see Table 1).

The specific form of the swelling curves attracts attention. While for the samples prepared in the presence of Zn oxide (see Fig. 1) the swelling curves reach saturation in ~5 hours (as is also the case for most of the usual vulcanizates), not less than a day is required for attainment of equilibrium with the magnesium and calcium samples in benzene (see Fig. 2), where after a period of rapid swelling a prolonged (about 15 hours), approximately linear increase in the volume of the samples is observed. This phenomenon was not observed on swelling of these same samples in benzene with added acetic acid.

*It should be noted that in vulcanizing with Mg and Ca oxides, 1% of Zn oxide was introduced in addition, which facilitated the formation of "thiuram" bonds. This circumstance did not introduce a substantial error into the calculation relating to the above-mentioned minimum activity of ZnO in forming "salt" bonds ($M_c \approx 50{,}000$ with 10% ZnO).

The circumstance mentioned permitted us to suggest that in the case of the samples vulcanized in the presence of MgO and CaO a gradual decrease occurs in the number of "salt" cross linkages, which are broken in the process of swelling.

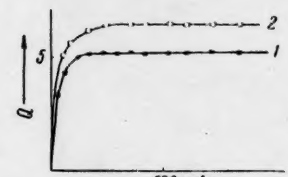


Fig. 1. Swelling curves for samples vulcanized in the presence of 2% thiuram and 10% ZnO. 1) In benzene, 2) in benzene with added acetic acid.

In the presence of such linkages the values of $M_c$ calculated from the maximum swelling values conform with the status of the dynamic equilibrium between breaking and newly forming bonds, which should change with a change in the temperature of the experiment. * Thus, the suggestion mentioned above could be verified by an investigation of the temperature relationship of swelling. The appropriate data are presented in Fig. 3, from which it follows that on raising the temperature of swelling to 65° the value of $M_c$ for the magnesium sample is considerably increased. Consequently, for carboxyl-containing polymers vulcanized with the help of magnesium oxide, certainly, the presence of the weak linkages mentioned is characteristic. A calculation of the energy of the bond E, made for these vulcanizates according to the Arrhenius equation, leads to values of 1000-2000 cals/mole, i.e., to values of the order of intermolecular forces.

It is characteristic that further increase in the temperature of the solvent – swelling in chlorobenzene and xylene at 125-130° – leads to complete solution of the above-mentioned vulcanizates, which under ordinary conditions have high physico-mechanical characteristics. Note that the values of E given correspond to the bond energy in a strained swollen network, weakened by the forces of reaction with the solvent and pressure on the network. The latter can be approximately evaluated by differentiating the expression for the elastic component of the entropy of swelling.

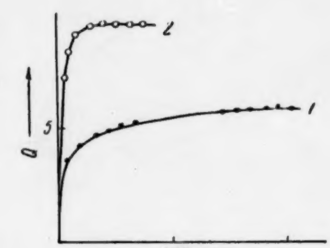


Fig. 2. Swelling curves for samples vulcanized in the presence of 2% thiuram and 5% MgO. 1) In benzene, 2) in benzene with added acetic acid.

The calculation leads to values of the order of $10^{-6}$ dyne per bond or $5 \times 10^{6}$ dynes/cm$^2$ when $Q \approx 10$, i.e., to values of the order of a lesser bond stability resulting from dispersion forces.

From what is stated above, it follows that vulcanization of carboxyl-containing polymers with metal oxides apparently has practically no relation to the formation of normal chemical bonds that correspond to the structure of neutral magnesium, calcium, and zinc salts of high molecular acids.


Fig. 3. Temperature relationship of swelling in benzene of a sample vulcanized in the presence of 10% MgO.

The suggestion first proposed by V. A. Kargin appears more probable, that is, that the genesis of the "salt" network takes place as a result of the formation of compounds of the type of basic salts, which as a consequence of poor solubility in the polymer either form crystalline agglomerates or remain bound with the coarse particles of the oxides distributed in the polymer.

In this case the stability of the vulcanization bonds should depend on the solubility of these salts in the polymer, and in particular should decrease with an increase in solubility.

* An increase in the temperature of swelling in the case of a stable vulcanization network should lead to some decrease in the extent of swelling, as a result of a diminution in the molar volume in comformance with equation (1). The value of $\mu$, close to 0.3, has little relation to the temperature.

Having selected the oleates of magnesium, calcium, and zinc and isooctane, as compounds to serve as models of a high molecular salt-polymer system, we established that the solubility of these salts decreased considerably in the order Mg>Ca>Zn (from 10.8 to 0.7 weight %). This fact confirms the point of view stated regarding the nature of the cross linkages formed on vulcanization of carboxyl-containing polymers with metal oxides, with these linkages apparently playing the role of unique "active fillers."

## LITERATURE CITED

[1] B. A. Dolgoplosk, E. I. Tiniakov, et al., Caoutchouc and Rubber, No. 3, 11 (1957).*

[2] B. A. Dolgoplosk and V. N. Reikh, et al., Caoutchouc and Rubber, No. 6, 1 (1957).*

[3] P. I. Flory and J. Rehner, J. Chem. Phys. 11, 512, 521 (1943).

S. V. Lebedev All-Union Scientific Research
Institute for Synthetic Rubber

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* In Russian.

# DOUBLE CHLORIDES OF ELEMENTS OF THE CERIUM GROUP WITH TRIMETHYLAMINE CHLORIDE

N. N. Sakharova and S. V. Zemskov

(Presented by Academician I. I. Cherniaev, January 24, 1958)

In due time the double chlorides [1] and nitrites [2] of the rare-earth elements of the cerium group with appropriate tetraphenylphosphonium salts have been investigated [3-5]. Later Medoks [6] isolated double nitrates of lanthanum, cerium, praseodymium, and neodymium with triphenylbenzylphosphonium.

The double salts of this group with the salts of organic bases mentioned were obtained from 96% ethyl alcohol; they were broken down by the action of water into the starting components; they had characteristic melting points and different solubilities in organic solvents and mixtures thereof.

Continuing work started earlier on the investigation of the double salts of the rare-earth elements with the salts of organic bases, we included in our series of studies the chlorides of methylamine, dimethylamine, and trimethylamine, as more readily available materials. It seemed to us not without interest to ascertain how complex formation proceeds in the presence of water and in nonaqueous media for chlorides of the rare-earth elements with the corresponding salts of the amines mentioned, in relation to their degree of substitution.

As starting materials for the preparation of the double chlorides of the rare-earth elements with trimethylamine we used lanthanum chloride (containing less than 1.6% praseodymium chloride), cerium chloride prepared from the repeatedly recrystallized double ammonium nitrate of tetravalent cerium, and chemically pure preparations of the chlorides of praseodymium and neodymium. The trimethylamine chloride had its characteristic melting point of 271°.

It was first established that the chlorides of lanthanum, cerium, praseodymium, and neodymium on combination with trimethylamine chloride in the presence of 96% ethyl alcohol yield several compounds, the formation of which is dependent on the relative amounts of the materials entering into the reaction and the conditions of the crystallization. Thus, with a molecular ratio of the rare-earth chlorides (calculated as the anhydrous salts) to trimethylamine chloride of 1 : 8, i.e., with an excess of the latter, compounds are obtained where there are four molecules of the amine to one atom of rare-earth metal.

To prepare these compounds, the chlorides of lanthanum, cerium, praseodymium, and neodymium and trimethylamine, taken in the ratio mentioned above, were dissolved separately by heating slightly in the minimum amounts possible of ethyl alcohol (approximately 2 ml per gram of starting material). The clear solutions obtained of the rare-earth chlorides and trimethylamine were mixed together warm. As the excess solvent was removed in a vacuum desiccator over calcium chloride and paraffin in 1-2 days, beautiful, well-formed crystals separated from the solution as hexahedral plates, colorless in the case of lanthanum and cerium, and colored green and violet in the case of praseodymium and neodymium. The crystals, which deliquesced slightly in the air, were quickly separated from the mother liquor, washed several times with cold ethyl alcohol, and dried under vacuum bell-jar at 50° and 4-5 mm in the presence of calcium chloride and phosphorus pentoxide.

The rare-earth metal content was determined in the dehydrated compounds by the oxalate method, with subsequent conversion of the oxalate to the corresponding oxides (with the exception of praseodymium, which does not give an oxide of exact chemical composition) of chlorine, nitrogen, carbon, and hydrogen.

Double chloride of lanthanum with trimethylamine. Anhydrous salt.

Found %: La 22.48. 22.50; Cl 39.20, 39.40; C 22.64; N 8.75, 9.03; H 6.70. $LaCl_3 \cdot 4(CH_3)_3N \cdot HCl$. Calculated %: La 22.08; Cl 39.60; C 22.96; N 8.93; H 6.43.

Double chloride of cerium with trimethylamine. Anhydrous salt.

Found %: Ce 22.32, 22.51; Cl 39.21, 39.30; N 8.68, 8.99; C 22.81, 23.12; H 6.74, 6.95. $CeCl_3 \cdot 4(CH_3)_3N \cdot HCl$. Calculated %: Ce 22.27; Cl 39.50; N 8.91; C 22.92; H 6.40.

Double chloride of praseodymium with trimethylamine. Anhydrous salt.

Found %: Cl 39.48, 39.80; C 22.98; N 8.57, 8.89; H 6.80. $PrCl_3 \cdot 4(CH_3)_3N \cdot HCl$. Calculated %: Cl 39.43; C 22.89; N 8.90; H 6.40.

Double chloride of neodymium with trimethylamine. Anhydrous salt.

Found %: Nd 22.86, 22.59; Cl 39.63, 39.58; N 8.99, 9.33; C 23.04; H 6.99. $NdCl_3 \cdot 4(CH_3)_3N \cdot HCl$. Calculated %: Nd 22.80; Cl 39.22; N 8.85; C 22.80; H 6.71.

The melting point of the double chlorides of the rare-earth elements with trimethylamine proved to be 287° for the lanthanum salt and 289, 295, and 296° for the corresponding compounds of cerium, praseodymium, and neodymium. Double recrystallization of the double chlorides obtained, with the exception of the lanthanum salt, did not result in any change in the melting point. The double chloride of lanthanum, synthesized from a preparation containing less than 1.6% of praseodymium chloride, acquired a stable melting point only after three recrystallizations from 96% ethyl alcohol. The yields of the double chlorides obtained varied within the limits 80 to 90%.

The double chlorides of lanthanum, cerium, praseodymium, and neodymium with trimethylamine were readily soluble only in water and methyl alcohol, poorly soluble in ethyl alcohol, and the solubility in this last solvent decreased regularly with the increase in melting point from the lanthanum salt to the neodymium salt; they were not soluble in ether, acetone, benzene, toluene, xylene, dichloroethane, chloroform, quinoline, pyridine, bromobenzene, or isobutyl or isoamyl alcohols.

Thus, as a result of the work carried out we obtained double chlorides of rare-earth elements with trimethylamine in the presence of 96% of ethyl alcohol, corresponding to the general formula $MeCl_3 \cdot 4(CH_3)_3N \cdot HCl$, where Me is La, Ce, Pr and Nd; the properties of these compounds have been studied and their solubility in water and organic solvents has been determined.

The investigation of similar double salts of rare-earth elements of the cerium group with salts of aliphatic and aromatic amines in the presence of water and nonaqueous media is being continued by us.

## LITERATURE CITED


[1] N. N. Sakharova, Proc. Acad. Sci. USSR, 77, 73 (1951).

[2] G. V. Medoks and N. N. Sakharova, Proc. Acad. Sci. USSR, 73, 1201 (1950).

[3] Ia. Ia. Dodonov and G. V. Medoks, Ber., 61, 907 (1928).

[4] G. V. Medoks, E. M. Soshestvenskaia and N. N. Sakharova, J. Appl. Chem. 25, 1111 (1952).*

[5] G. V. Medoks and N. N. Sakharova, Manual Western Saratov State Univ., 34, 117 (1954).

[6] G. V. Medoks, J. Gen. Chem. 26, 382 (1956).*



N. G. Chernyshevskii Saratov State University



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# SYNTHESIS OF HIGH MOLECULAR WEIGHT HYDROCARBONS OF COMPOUND STRUCTURE

Š. R. Sergienko, L. N. Kvitkovskii, A. L. Tsedilina, and Al. A. Petrov

(Presented by Academician B. A. Arbuzov, January 4, 1958)

Systematic studies on the synthesis of individual hydrocarbons and the investigation of their properties and reactions lie at the basis of recently developed new and very effective methods of analysis of hydrocarbon mixtures. Among such new methods are, first of all, the spectral methods (Taman spectra, infrared, and ultraviolet spectroscopy).

At the present time the most essential problem is the investigation of the composition, structure, and properties of the highest molecular weight fraction of petroleum, which, as a rule, comprises more than half of the crude petroleum. The method of separation of the individual compounds, which has been used successfully in the investigation of the light and medium fractions of petroleums, although it can be used in isolated cases for the solution of exceptional problems, is difficult and not very efficient for the study of the composition and properties of complex mixtures of the high molecular weight compounds of petroleum.

In this case we may expect the most success from the use of the principles on which physico-chemical analysis is based, i.e., the establishment of quantitative relationships of the basic physical properties of the whole complex system to its chemical composition. But the successful use of this principle requires that the relationship of the properties to the composition of the system be determined simultaneously both in the natural complex system of unknown structure and in artificial mixtures made up from the individual compounds, i.e., in mixtures that serve as a known standard for the natural systems under investigation. Precisely this principle is the basis of the numerous modifications of the method for the structural group composition of the oily fractions of petroleum.

The molecules of the high molecular weight compounds of petroleum ($C_{20}$ and higher), as investigations in recent years have shown, have predominantly a complex (hybrid) structure. In other words, structural members of various homologous series (paraffins, cycloparaffins, benzene, naphthalene, etc.) participate to greater or lesser degree in the construction of the molecule. The proportion of structural elements of aliphatic and aromatic nature varies within wide limits, depending on the chemical nature of the petroleum. In this connection it was decided to synthesize a series of hydrocarbons of the composition $C_{24}-C_{32}$, which had not been described in the literature, with a different proportion of the carbon atoms in the structural members of the molecule.

The hydrocarbons that have now been prepared and also their properties are given in Table 1.

We are planning further both the synthesis of new structures and a more detailed study of the properties of the hydrocarbons synthesized, including the viscosity-temperature characteristics, adsorption properties, ultraviolet and infrared spectra, etc. There is no doubt that a detailed study of the properties and reactions of these compounds will contribute to the more rapid investigation of the composition and structure of the high molecular weight compounds of petroleum.

In conclusion, let us dwell briefly on several details of the synthesis of the hydrocarbons. The tertiary alcohols, prepared by the Grignard method, were dehydrated in vacuo over pure aluminum oxide at 280-320° and 1 mm residual pressure. Hydrogenation of the products was carried out in an autoclave in the presence of Raney nickel. Hydrogenation conditions: double bond 50-70°; benzene ring 150°; naphthalene ring in decalin 150°, in tetralin 100°; pressure in all cases 100-150 atm.

TABLE 1

| Expt. No. | Hydrocarbon | B. p., °C | $n_D^{20}$ | $d_4^{20}$ | Method of preparation |
|---|---|---|---|---|---|
| 1 | 1,1-diphenyldodecane | 208 | 1.5241 | 0.9248 | From phenylmagnesium bromide and ethyl laurate |
| 2 | 1,1-dicyclohexyldodecane | 204 | 1.4803 | 0.8758 | Hydrogenation of hydrocarbon No. 1 |
| 3 | 2,11-diphenyldodecane | 200 | 1.5212 | 0.9244 | From 1,10-diphenyldecanedione-1,10 and methylmagnesium iodide. Ketone synthesized from sebacic acid dinitrile and phenylmagnesium bromide. |
| 4 | 2,11-dicyclohexyldodecane | 196 | 1.4802 | 0.8759 | Hydrogenation of hydrocarbon No. 3 |
| 5 | 1,5-diphenyl-3-heptylpentane | 210 | 1.5206 | 0.9233 | From the organomagnesium compound of the bromide of phenylethyl alcohol and ethyl caprylate |
| 6 | 1,5-dicyclohexyl-3-heptylpentane | 208 | 1.4776 | 0.8691 | Hydrogenation of hydrocarbon No. 5 |
| 7 | 1-phenyl-1-cyclohexyldodecane | 206 | 1.4980 | 0.8960 | From laurophenone and cyclohexylmagnesium bromide. Ketone synthesized from phenylmagnesium bromide and lauronitrile. |
| 8 | 1,1-bis(α-dinaphthyl) dodecane | 254 | 1.5989 | 1.0130 | From naphthylmagnesium bromide and ethyl laurate |
| 9 | 1,1-bis(α-decahydronaphthyl)dodecane | 252 | 1.5245 | 0.9537 | Hydrogenation of hydrocarbon No. 8 |
| 10 | 1,1-bis(α-tetrahydronaphthyl)dodecane | 243 | 1.5480 | 0.9796 | Hydrogenation of hydrocarbon No. 8 |
| 11 | 1-(α-naphthyl)-1-(β-decahydronaphthyl)-dodecane | 252 | 1.5500 | 0.9662 | From lauronaphthone and decalinmagnesium bromide. Ketone was prepared simultaneously with hydrocarbon No. 8 |
| 12 | 1,3-bis(α-naphthyl)-2-nonylpropane | 248 | 1.5780 | 1.0044 | From methylnaphthylmagnesium chloride and ethyl caprate |
| 13 | 1,3-bis(α-decahydronaphthyl)-2-nonylpropane | 244 | 1.5013 | 0.9263 | Hydrogenation of hydrocarbon No. 12 |
| 14 | 2,11-bis(α-naphthyl)-dodecane | 259 | 1.5960 | 1.0193 | From 1,10-dinaphthyldecanedione-1,10 and methylmagnesium iodide. Ketone synthesized from sebacic acid dinitrile and naphthylmagnesium bromide. |
| 15 | 2,1 1-bis(α-decahydronaphthyl)dodecane | 256 | 1.5135 | 0.9484 | Hydrogenation of hydrocarbon No. 14 |

*Boiling points obtained at the following pressures: for hydrocarbons No. 1-7 at 4 mm Hg, for hydrocarbons No. 8-15 at 0.5 mm Hg.

The hydrocarbons prepared of the composition $C_{24}$ were distilled on a special cap vacuum column with an efficiency of 16 theor. plates. The hydrocarbons of the composition $C_{32}$ were purified by molecular distillation at a pressure of $1 \cdot 10^{-5}$ and a temperature of 170°.

It also should be noted that most of the compounds synthesized by us solidified as a glass on cooling at a temperature from −20 to −30° (hydrocarbons of the composition $C_{24}$). However, 1,1-dicyclohexyldodecane, after standing for a half year, unexpectedly crystallized at room temperature (m. p. +27°). It is impossible to exclude the possibility of the crystallization of other hydrocarbons also, which compels us to approach carefully the appraisal of the vitrification of these and other structures. This problem will defined by us further.

Petroleum Institute of the Academy
of Sciences USSR

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# COLOR PHENOMENA IN DIACYL DERIVATIVES OF p-AMINOPHENOL

E. A. Smirnov

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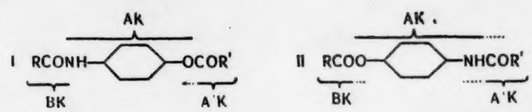
In previous communications [1] we have shown that when two different electron donor systems* (AK and A'K) are present in a compound simultaneously with an electronophilic system** (BK) that is not connected with the former by a chain of conjugated double bonds, this compound may sometimes be obtained in two differently colored forms. The existence of the latter is explained by the fact that direct reaction of the electrophilic and the electron donor systems with the aid of extramolecular forces [2], which is a basic factor determining the coloration of "compounds with separate chromophoric systems,"*** in this case can be brought about in two ways: either the electrophilic system reacts with the electron donor system AK or with the system A'K.

In the present communication, compounds are considered with structures of types I and II. In these compounds the electrophilic system (BK) is the acyl group of 4-nitrobenzoic or 3,5-dinitrobenzoic acid (RCO), the electron donor system AK is the p-aminophenol molecule (diacylated), and the electron donor system A'K is the acyl group of trimethylgallic acid (R'CO).




From Table 1 it can be seen that almost all the diacyl derivatives of p-aminophenol (with the exception of No. 2) that contain the system A'K form two colored forms: a weakly colored, pale yellow form (a) and a more deeply colored yellow form (b). The two forms can be converted into one another by crystallization from different solvents (see experimental section), whereupon this conversion sometimes takes place very obviously. Thus, for example, the pale yellow form of compound No. 4 isolated from acetone becomes noticeably yellower even when simply treated with alcohol; the pale yellow form of compound No. 6 starts to turn yellow even in the acetone mother liquor. In compounds that do not contain the electron donor system A'K it was not possible in even one instance to obtain two differently colored forms. From this it can be concluded that the possibility of the existence of the compounds under consideration as more deeply colored forms is connected with the presence in them of the system A'K. This system contains three $OCH_3$ groups, the electron donor effect of which is weakened by the presence in it of the CO group. But since the electrophilic effect of the latter is to a considerable degree suppressed by the addition to it of an NH- or OH-group, its influence on the electron donor system A'K should be small. It therefore may be considered that the system A'K is a more strongly electron-donating system than AK, because in the latter the donor properties of both the amino and the hydroxyl group

*The electron donor system is a conjugated chain of double bonds with the addition of an electron donor group ($NH_2$, OH, etc.).

**A conjugated chain of double bonds with the addition of an electrophilic group (CO, $NO_2$, etc.).

***In other words, compounds in which the electrophilic and electron donor system are not connected together by conjugated double bonds.

are to a considerable degree suppressed by the CO groups added to them. Further it is necessary to keep in mind that the system A'K is not conjugated with the system BK, and therefore the reaction of these systems, which provides the conditions for the deeper coloration of form (b), can be brought about only with the aid of extramolecular forces.

The presence of color, although weaker, in compounds having only one electron donor system AK, indicates that the system BK can react with the system AK. In compounds of type I a similar possibility is so much the more likely because here this reaction can be brought about not only with the aid of extramolecular forces, but in some measure also through the chain of conjugated double bonds that is formed as a result of the tautomerism of the CONH group [3]. The similarity of the color of the compounds that have one electron donor system (AK) to the color of the compounds that have both electron donor systems, furnishes a basis for considering that the color of the weakly colored form of the latter is also a result of the reaction between the systems BK and AK, with a disruption of the reaction between BK and A'K.

It is further interesting to note that in almost all instances the weakly colored forms of the compounds that contain the acyl group of benzoic acid are colored somewhat more deeply than the corresponding compounds containing the acyl group of trimethylgallic acid, as is especially noticeable in compounds of type II.

Comparison of the color of compounds of type I and II shows that the latter, as a rule, are colored somewhat more deeply than the former. The explanation of this can be found if we proceed from an analysis of the relative "strength" of the reacting systems in the two cases. System BK is stronger in compounds of type I because the OH group weakens the electrophilic properties of the CO group to a lesser degree than does the amino group. For the same reason the system A'K also appears to be stronger in compounds of type II. The systems AK of compounds of type I and II do not differ significantly in strength.

## EXPERIMENTAL

N-(4-Nitrobenzoyl)-0-benzoyl-p-aminophenol (Table 1, No. 1). A mixture of N-(4-nitrobenzoyl)-p-aminophenol [4] (1 mole) and benzoyl chloride (4 moles) dissolved in nitrobenzene was heated for a half-hour almost to boiling. The reaction product was recrystallized from pyridine. Greenish, lamellar crystals with m. p. 276-277°, difficultly soluble in the usual organic solvents, comparatively easily soluble in pyridine were produced.

Found %: N 7.77. $C_{20}H_{14}O_5N_2$. Calculated %: N 7.76.

N-(4-Nitrobenzoyl)-0-(3,4,5-trimethoxybenzoyl)-p-aminophenol (Table 1, No. 2).

It was prepared as the preceding compound. It was recrystallized from pyridine and then from a mixture of pyridine and methanol (1 : 1). Slightly greenish crystals with m. p. 246-247°, rather soluble in pyridine, more difficultly soluble in acetone and dichloroethane, difficultly soluble in alcohol, were produced.

Found %: N 6.15. $C_{23}H_{20}O_8N_2$. Calculated %: N 6.20.

N-(3,5-Dinitrobenzoyl)-0-benzoyl-p-aminophenol (Table 1, No. 3). It was prepared from N-(3,5-dinitrobenzoyl)-p-aminophenol [5] and benzoyl chloride by the Schotten-Baumann reaction. It was recrystallized from acetone and then from alcohol. Long, narrow plates of a pale yellow color with m. p. 226-226.5° rather easily soluble in acetone, more difficultly soluble in alcohol and benzene, were produced.

Found %: N 10.43. $C_{20}H_{13}O_7N_3$. Calculated %: N 10.32.

N-(3,5-Dinitrobenzoyl)-0-(3,4,5,-trimethoxybenzoyl)-p-aminophenol (Table 1, No. 4). This and the following preparations were obtained in a manner similar to the preceding ones. It was recrystallized twice from acetone, as pale yellow prismatic crystals with m.p. 218-219°. On treatment with alcohol the material turned yellow and it separated from alcohol solution as a bright yellow form with the same melting point. A very yellow form was separated from dichloroethane as rhombic crystals. On recrystallization from acetone or toluene, the yellow form again was converted to the pale yellow. The latter turned yellow on storage. Both forms were readily soluble in acetone and dichloroethane, rather readily in toluene, more difficultly in alcohol.

Form (a) Found %: N 8.48. $C_{23}H_{19}O_{10}N_3$. Calculated %: N 8.45.

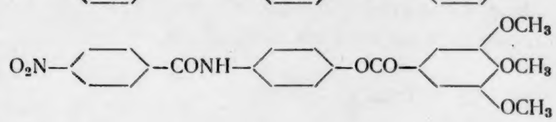
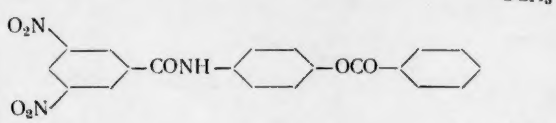
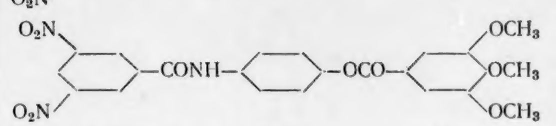
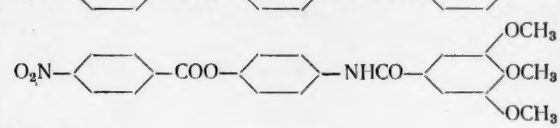
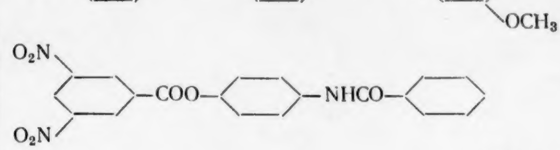
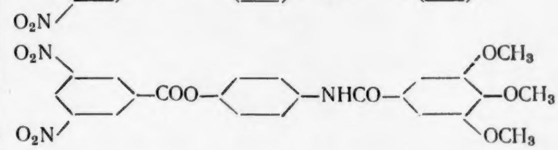
Form (b) Found %: N 8.37. $C_{23}H_{19}O_{10}N_3$. Calculated %: N 8.45.

N-Benzoyl-0-(4-nitrobenzoyl)-p-aminophenol (Table 1, No. 5). Starting materials: N-benzoyl-p-aminophenol and p-nitrobenzoyl chloride. Recrystallized twice from pyridine as greenish-yellow crystals with m. p. 285-286°, difficultly soluble in the usual organic solvents, comparatively easily in pyridine.

Found %: N 7.75. $C_{20}H_{14}O_5N_2$. Calculated %: N 7.76.

TABLE 1

Color of Diacyl Derivatives of p-Aminophenol

| Expt. No. | Formula of compound | Color of material in crystals | |
|---|---|---|---|
| | | form (a) | form (b) |
| 1 |  | greenish | — |
| 2 |  | slightly greenish | — |
| 3 |  | pale yellow | — |
| 4 |  | » | bright yellow |
| 5 |  | greenish yellow | — |
| 6 |  | pale yellow | bright yellow |
| 7 |  | greenish yellow | — |
| 8 |  | pale yellow | yellow |

N-(3,4,5-Trimethoxybenzoyl)-0-(4-nitrobenzoyl)-p-aminophenol (Table 1, No. 6). Starting materials: N-trimetholybenzoyl -p-aminophenol and p-nitrobenzoyl chloride. Recrystallized from acetone and then from alcohol as bright yellow crystals with m. p. 218.5-219.5°. From dichloroethane, and even better from a mixture of dichloroethane and benzene, a pale yellow form separated as fine, fibrous crystals with the same melting point.

Form (a) Found %: N 6.28. $C_{23}H_{20}O_8N_2$. Calculated %: N 6.20.

Form (b) Found %: N 6.34. $C_{23}H_{20}O_8N_2$. Calculated %: N 6.20.

N-Benzoyl-0-(3,5-dinitrobenzoyl)-p-aminophenol (Table 1, No. 7). Starting materials: N-benzoyl-p-aminophenol and 3,5-dinitrobenzoyl chloride. The product was recrystallized from acetone as greenish-yellow tablets with m. p. 222-223°, readily soluble in pyridine, rather readily in acetone, more difficultly in dichloroethane and toluene, difficultly in alcohol.

Found %: N 10.39. $C_{20}H_{13}O_7N_3$. Calculated %: N 10.32.

N-(3,4,5-Trimethoxybenzoyl)-0-(3,5-dinitrobenzoyl)-p-aminophenol (Table 1, No. 8). Starting materials: N-trimethoxybenzoyl-p-aminophenol and 3,5-dinitrobenzoyl chloride. Part of the product was recrystallized from acetone, another part from alcohol and then from dichloroethane. From acetone a yellow form separated with m. p. 211-211.5°; from dichloroethane a pale yellow form separated as silky crystals with the same melting point. Upon crystallization from dichloroethane it was necessary to seed appropriately (with the pale yellow form); otherwise a mixture of both forms separated, or sometimes the yellow one. The latter was obtained well from acetic acid. Both forms were rather easily soluble in dichloroethane and acetone, more difficultly in toluene and alcohol.

Form (a) Found %: N 8.53. $C_{23}H_{19}O_{10}N_3$. Calculated %: N 8.45.

Form (b) Found %: N 8.47. $C_{23}H_{19}O_{10}N_3$. Calculated %: N 8.45.

N-(3,4,5-Trimethoxybenzoyl)-p-aminophenol. It was prepared similarly to the nitrobenzoyl derivative of p-aminophenol [5]. Recrystallized twice from dilute alcohol as rhombic crystals with m. p. 231.5-232.5°, readily soluble in acetone, alcohol, and benzene, considerably more difficultly in water.

Found %: N 4.79. $C_{16}H_{17}O_5N$. Calculated %: N 4.62.

## LITERATURE CITED


[1] E. A. Smirnov, J. Gen. Chem. No. 2, 1394 (1953); J. Gen. Chem. 27, 2682 (1957).*

[2] V. A. Izmail'skii and P. A. Colodkov, Proc. Acad. Sci. USSR, 60, 587 (1948).

[3] E. A. Smirnov, J. Gen. Chem. 25, 1018 (1955); 27, 1922 (1957).*

[4] V. A. Izmail'skii and E. A. Smirnov, J. Gen. Chem. 7, 520 (1937); Bull. Soc. Chim. (5), 4, 91 (1937).

[5] E. A. Smirnov, J. Gen. Chem. 10, 1382 (1940).



I. M. Gubkin Moscow Petroleum
Institute of the Academy of Sciences USSR



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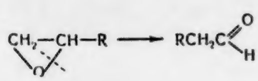
# ISOMERIZATION OF $\gamma$-OXIDES (TETRAHYDROFURANS) TO ALIPHATIC CARBONYL COMPOUNDS

Member-Correspondent of Acad. Sci. USSR N. I. Shuikin and I. F. Bel'skii

Various chemical transformations of alkylene oxides are connected with the easy opening of an $\alpha$-oxide ring under the influence of different agents. Among the thoroughly studied reactions of the $\alpha$-oxide series is their isomerization to aliphatic carbonyl compounds. This reaction occurs upon heating up to 300-500° or at lower temperatures in the presence of catalysts (aluminum oxide, phosphoric acid, metal phosphates, silicates, etc.).

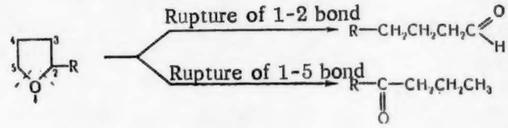
Unsymmetrical $\alpha$-oxides that have one or two alkyl substituents on one carbon atom of the ring (propylene oxide, isobutylene oxide) are isomerized with opening of the ring predominantly at the bond connecting the oxygen atom with that carbon atom on which the substituent is, resulting in the formation of aldehydes [1]:



Up to now a similar isomerization has not been known in the $\gamma$-oxide series (tetrahydrofurans). The catalysts that are most active in the isomerization of $\alpha$-oxides lead in the case of tetrahydrofuran and its homologs to dehydration with the formation of dienes and aromatic hydrocarbons. Thus, for example, it has been shown that tetrahydrosylvan, in contact with $Al_2O_3$, $TiO_2 \cdot Al_2O_3$, aluminum phosphate, or a mixture of phosphoric and boric acids, undergoes dehydration in the vapor phase to pentadiene [2-5]. The behavior of tetrahydrofuran and some of its derivatives (tetrahydrosilvan, tetrahydrofuryl alcohol) has been investigated under conditions of catalytic hydrogenation for the purpose of explaining the mechanism of hydrogenolysis of the furan ring. It was found that on a platinum catalyst in the liquid phase tetrahydrofuran and tetrahydrofuryl alcohol do not undergo any change [6].

We have investigated the conversions of tetrahydrofuran and its $\alpha$-substituted homologs on platinized carbon in the vapor phase at 230-250° and found that under these conditions the tetrahydrofuran and its homologs are isomerized with opening of the ring at the C—O bonds to aliphatic carbonyl compounds.

The isomerization of $\alpha$-alkyltetrahydrofurans with opening of the ring should lead in general to the formation of an aldehyde or ketone depending on which of the two C—O bonds undergoes cleavage:




The sole isomerization product of tetrahydrofuran should be n-butylraldehyde. However, under the conditions of carrying out the isomerization, neither tetrahydrofuran itself nor its $\alpha$-substituted homologs gave

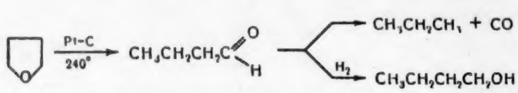
practically appreciable amounts of aldehydes. Tetrahydrofuran on platinized carbon at 250° yielded a mixture of carbon monoxide and propane; from tetrahydrosilvan, α-ethyl- and α-propyltetrahydrofuran the corresponding ketones were obtained under these conditions as the principal products, and also a considerably smaller amount of carbon monoxide and n-butane, n-pentane, and n-hexane. The formation from tetrahydrofurans of carbon monoxide and paraffinic hydrocarbons is a result of a secondary decarbonylation of the aldehydes that are obtained from isomerization:

$$R-CH_2CH_2CH_2C\begin{smallmatrix}\nearrow O\\ \searrow H\end{smallmatrix} \longrightarrow R-CH_2CH_2CH_3 + CO.$$

Actually, the aldehydes are very easily decarbonylated on platinized carbon in the vapor phase to the corresponding hydrocarbons. Thus, we found that when heptanol-1 was passed over Pt-C at 250° in the absence of hydrogen, n-hexane and carbon monoxide were formed instead of the aldehyde. Under the same conditions benzaldehyde and benzyl alcohol are converted to benzene.

Thus, the relative amounts of ketones and alkanes produced in the conversions of α-alkyltetrahydrofurans show to what degree splitting of the 1-5 and the 1-2 C—O bonds respectively occurs upon isomerization of the γ-oxide ring. As a result of the experiments carried out,it was found that the α-alkyltetrahydrofurans that have in the side chain a methyl, ethyl, or propyl group are isomerized on Pt-C chiefly to aliphatic ketones in 90-95%.yield calculated on the α-alkyltetrahydrofuran transformed; the isomerization of the γ-oxide to the aldehyde with opening of the ring at the 1-2 C—O bond, next to the alkyl radical, occurs to an insignificant degree (5-10%).

The isomerization of alkyltetrahydrofurans to aliphatic carbonyl compounds is irreversible, since it is possible completely to convert the starting γ-oxide to the corresponding ketone and hydrocarbon. Thus, after twice passing tetrahydrosilvan over Pt—C at 250° with a volume velocity of 0.1 hour$^{-1}$ the liquid catalyzate contained a mixture of approximately equal amounts of pentanone-2 and unconverted tetrahydrosilvan; α-ethyl-tetrahydrofuran passed over the same catalyst with the same volume velocity, but four times consecutively, yielded 95% of hexanone-3 and only about 5% of n-pentane. If the isomerization of the γ-oxides is carried out in a current of hydrogen, also over platinized carbon, a secondary hydrogenation of the carbonyl compounds formed, to the corresponding alcohols, takes place. Thus, when tetrahydrofuran mixed with hydrogen is passed over Pt—C at 240°, a liquid catalyzate is obtained which contains, along with unchanged tetrahydrofuran, about 20% of n-butyl alcohol, while under these same conditions but in the absence of hydrogen, tetrahydrofuran produces only a mixture of gaseous products — propane and carbon monoxide. This conversion can be expressed by the following scheme:




α-Propyltetrahydrofuran passed in a current of hydrogen over Pt-C at 235-240° with a volume velocity of 0.1 hour$^{-1}$ yielded a mixture of heptanone-4 and heptanol-4 with yields of 78 and 18% respectively, calculated on the σ-propyltetrahydrofuran converted, and a little n-hexane.

For purposes of comparison we carried out the isomerization of propylene oxide under the same conditions as the isomerization of the alkyltetrahydrofurans. The conversion after one passage with volume velocity of 0.1 hour$^{-1}$ was about 30-40%. This shows that the α-oxide ring is isomerized over Pt—C to carbonyl compounds somewhat more easily than the γ-oxide ring. The formation of gaseous products was much more considerable than in the isomerization of the alkyl tetrahydrofurans. The liquid catalyzate contained, besides unchanged propylene oxide, acetone (95%) and propionaldehyde (4%) calculated on the α-oxide converted. These results show that platinized carbon to a greater extent than other catalysts [1] promotes the isomerization of unsymmetrical α-oxides to aliphatic ketones.

## EXPERIMENTAL

Starting materials. Pure tetrahydrofuran was isolated from the technical product by distillation on an efficient column in the presence of sodium. α-Methyl-, α-ethyl-, and α-propyltetrahydrofurans were prepared by hydrogenation of the corresponding alkyl furans on palladized carbon in the vapor phase at 130-150°. The properties of tetrahydrofuran and its homologs are given in Table 1.

TABLE 1

Properties of Tetrahydrofuran and Its Homologs

| Tetrahydrofurans | B. p., °C/mm Hg | $d_4^{20}$ | $n_D^{20}$ |
|---|---|---|---|
| Tetrahydrofuran | 65—66°/755 | 0.8886 | 1.4070 |
| Tetrahydrosilvan | 79—79.2°/750 | 0.8582 | 1.4060 |
| α-Ethyltetrahydrofuran | 106.5—107°/742 | 0.8556 | 1.4163 |
| α-Propyltetrahydrofuran | 131.5—132.5°/750 | 0.8562 | 1.4232 |

Catalyst. Platinized carbon containing 15% platinum was prepared by impregnating activated carbon with a solution of chloroplatinic acid and its subsequent reduction in a glass tube at 250-300°.

Isomerization of γ -oxides was carried out in the vapor phase at 235-250°. In each experiment 50 g of material was taken, which was passed over the catalyst in a mixture with hydrogen or without it at a volume velocity of 0.1 $hour^{-1}$. The dried catalyzates were subjected to distillation on a column with an efficiency of 40 theoretical plates. The gaseous products of the reaction were analyzed in an Orsat-Lunge apparatus for their content of carbon monoxide and in a chromathermograph where the composition and the content of saturated hydrocarbons were determined.

The properties of the products obtained by isomerization of the γ -oxides in the presence of hydrogen or without it are given in Table 2.

TABLE 2

Properties of Products of the Isomerization of γ -Oxides

| Isomerization products | B. p., °C/750 mm Hg | $d_4^{20}$ | $n_D^{20}$ |
|---|---|---|---|
| Butanol-1 | 116 —117 | 0.8186 | 1.4004 |
| Pentanone-2 | 101 —102 | 0.8081 | 1.3905 |
| Hexanone-3 | 123 —124 | 0.8169 | 1.4006 |
| Heptanone-4 | 142.5—143 | 0.8176 | 1.4085 |
| Heptanol-4 | 153 —155 | 0.8213 | 1.4198 |

Conclusions. 1. It has been established that the γ -oxide (tetrahydrofuran) ring is capable of being isomerized in the vapor phase on platinized carbon with cleavage of the ring at the C—O bonds, as a result of which aliphatic carbonyl compounds are formed.

2. When an alkyl radical ($CH_3$, $C_2H_5$, n-$C_3H_7$) is present in the α-position of the tetrahydrofuran ring, isomerization of the γ -oxide proceeds chiefly (90-95%) with the opening of the ring at the C—O bond most removed from the side substituent, which leads to the formation of the corresponding aliphatic ketones.

3. The aldehydes formed in small amount upon isomerization of tetrahydrofuran and α-alkyltetrahydrofurans with cleavage at the 1-2 C—O bond undergo decarbonylation under the reaction conditions to the corresponding paraffinic hydrocarbons.

## LITERATURE CITED

[1] V. Leontovich, Ber. 36, 2016 (1903).

[2] A. Burnette, Rubb. Chem. Technol. 18, 284 (1945).

[3] U. deMelle and H. Guinot, French Pat., 811695 (1936); Chem. Zbl. 2, 1680 (1937).

[4] U. deMelle, French Pat. 942088 (1949); Chem. Abstr. 45, 632 (1951).

[5] N. I. Shuikin and I. F. Bel'skii, Bull. Soc. Chim. No. 11-12 (1956).

[6] W. Kaufmann and R. Adams, J. Am. Chem. Soc. 45, 3029 (1923).

[7] H. Smith and J. Fuzek, J. Am. Chem. Soc. 71, 415 (1949).

N. D. Zelinskii Institute of Organic
Chemistry of the Academy of Sciences USSR

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# CATALYTIC CONVERSIONS OF 2-METHYLTHIOPHENE IN THE PRESENCE OF STEAM

Academician A. A. Balandin, L. I. Sovalova and T. A. Slovokhotova

It would naturally be supposed that the catalytic dealkylation reaction in the presence of steam, which is general for a whole series of classes of chemical compounds [1-5], would extend to derivatives of thiophene. It is reasonable that during a study of this problem, difficulties would arise in connection with the specific behavior of thiophene derivatives over metallic catalysts in the presence of hydrogen [6-11], which is one of the products of the demethylation reaction.

Our work was carried out over $Ni/Al_2O_3$ and $Co/Al_2O_3$ catalysts. The temperature limits and the mole ratios of water to the substance studied ($\omega$) were selected on the basis of these limits in demethylation reactions of other classes of chemical compounds (a temperature of from 200 to 425°; $\omega$ from 27 to 177).

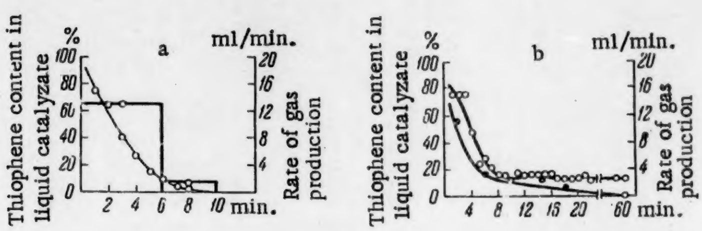


Fig. 1. Rate of gas production and of thiophene content in the reaction products as functions of time on the catalyst. a) Experiment No. 59; b) Experiment No. 60. Solid points – thiophene; circles – gas.

When thiophene was passed over the catalyst under these conditions, including a temperature of 425°, it was all recovered unchanged. The evolution of gas was not observed, and the catalyst remained capable of dehydrogenating cyclohexane. 2-Methylthiophene under these same conditions split off a methyl group and, to a lesser extent, underwent ring cleavage, which conforms to the conclusion as to the higher activity, in comparison with benzene and pyridine, of toluene and 2-picoline in reactions in which the benzene and pyridine rings are opened [2, 5]. The presence of methyl side chains gives the ring system greater reactivity.

The rate of production and the composition of the products of the reaction of 2-methylthiophene with water varied with time (see Fig. 1 and Table 1) when the vapors of these two compounds were passed over fresh catalyst. The rate of gas formation decreased at first and then reached a constant value which, other conditions being equal, was determined by the temperature and mole ratio of water to 2-methylthiophene. The liquid catalyzate contained thiophene during the first minutes of the experiment, but the amount decreased to zero when the rate of gas production reached a constant value. In the initial period of the reaction, the gas contained carbon dioxide in an amount which exceeded the amount of saturated hydrocarbons. When the rate of gas formation became constant, the amount of carbon dioxide decreased practically to zero, and the amount of saturates became appreciable; unsaturated hydrocarbons and hydrogen sulfide appeared above 400°.

Over the nickel catalyst, the amount of thiophene formed at corresponding times from the beginning of the experiment increased with temperature and decreased with an increase in the amount of water. The cobalt catalyst acted in a generally analogous manner.

TABLE 1

| Expt. No. | Catalyst | $\omega$ | Temperature(°C) | Average sample taken at indicated time from beginning of experiment (min) | Gas composition, (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $CO_2$ | saturated hydrocarbons | unsaturated hydrocarbons | $H_2S$ | $H_2$ |
| 62 | $Ni/Al_2O_3$ (1 : 2) | 48 | 359 | 10 | 3.1 | 1.3 | 0.0 | 0.0 | 95.6 |
| 60 | | 48 | 355 | 60 | 0.7 | 3.1 | 0.0 | 0.0 | 96.2 |

An increase in the reaction temperature increased the rate of gas production, while an increase in the amount of water decreased it. At the same time, an increase in the amount of water ($\omega$ = 177 as against 48) brought about an increase in the relative content of carbon dioxide in the gaseous products, evidently owing to a secondary reaction of the saturated hydrocarbons with the water.

TABLE 2

| Expt. No. | Catalyst | Regeneration time | $\omega$ | Temperature (°C) | Thiophene content, % | Gas composition (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $CO + CO_2$ | saturated hydrocarbons | unsaturated hydrocarbons | $H_2S$ | $H_2$ |
| 47 | $Ni/Al_2O_3$ (1 : 2) | 1.0 | 177 | 200 | 0 | 25 | 50 | 0.0 | 0.0 | 25 |
| 48 | Same | 1.0 | 177 | 328 | 2 | 21 | 30.5 | 0.0 | 0.0 | 48.5 |
| 50 | " " | 1.0 | 48 | 255 | 5.6 | 3.6 | 6.1 | 0.0 | 0.0 | 90.3 |
| 52 | " " | 1.0 | 48 | 365 | 30 | 4.3 | 6.7 | 0.0 | 0.0 | 89.0 |
| 53 | " " | 1.0 | 48 | 411 | 39 | 11.8 | 0.85 | 2.8 | 4.7 | 79.85 |
| 56 | " " | 1.0 | 48 | 393.5 | 38 | 9.6 | 3.0 | 0.0 | 0.0 | 87.4 |
| 63 | " " | 1.0 | 48 | 361 | 30 | — | — | — | — | — |
| 54 | " " | 3.0 | 48 | 285 | 35 | 3.2 | 4.5 | 0.0 | 0.0 | 92.3 |
| 55 | " " | 3.0 | 48 | 334 | 53 | 3.2 | 5.5 | 0.8 | 0.0 | 90.5 |
| 58 | $Ni/Al_2O_3$(1 : 1) | 1.0 | 48 | 250 | 56 | — | — | — | — | — |
| 65 | $Co/Al_2O_3$(1 : 1) | 3.0 | 27.3 | 364 | — | 5.8 | 0.9 | 1.7 | 0.0 | 91.6 |

The dependence of the composition of the liquid and gaseous reaction products on the temperature, the amount of water, and the catalyst composition is shown in Table 2 (an average sample of the liquid was collected for analysis after the first 4-6 minutes of an experiment, and the gas samples were collected after the first 10-15 minutes). The figures for thiophene content give its content, in per cent, in the mixture of thiophene and unreacted methylthiophene.

The activity of the catalyst with respect to the demethylation reaction, if it had not been lost completely, was restored by heating the catalyst for an hour in hydrogen. Longer heating increased the activity of the catalyst for this reaction (Table 3).

The material presented above permits the conclusion that methylthiophene, like methylpyridine, toluene, and xylene, undergoes demethylation in the presence of water over $Ni/Al_2O_3$ or $Co/Al_2O_3$ catalyst (1).

The accompanying complete decomposition of the methylthiophene molecule occurred both in the presence of water and in the presence of hydrogen (3), which is a product of the first two reactions.

Denoting the radical  by T, the reactions occurring may be formulated thus:

$$TCH_3 + 2H_2O = TH + CO_2 + 5H_2,$$
$$TCH_3 + 10H_2O = 5CO_2 + 12H_2 + H_2S, \quad (1)$$
$$TCH_3 + 4H_2 = C_5H_{12} + H_2S, \quad (2)$$
$$\left.\begin{aligned} TCH_3 + H_2 &= TH + CH_4, \\ TH + 4H_2 &= C_4H_{10} + H_2S. \end{aligned}\right\} \quad (3)$$

Reactions (1) and (2) proceed on the active centers of the metal catalyst (Ni, Co). The hydrogen sulfide formed by reaction (2) is not evolved at first; it poisons the surface of the catalyst by forming sulfides. Therefore, the rates of reactions (1) and (2) continuously decrease. At the same time, with an increase in the fraction of the active surface of the catalyst occupied by the metal sulfide, the selectivity for reactions (3) increases, these reactions occurring under the influence of hydrogen. Finally, when the surface is completely covered with sulfide, a steady state is established in the process. The composition of the products in this stage of the reaction differs from the product composition in the first stage. $H_2S$ appears in the gas; i.e., the demethylation reaction on the metal surface changes to a desulfurization reaction on the sulfides.

The amount of 2-methylthiophene reacting by reactions (3) increases with an increase in temperature, as is indicated by the increase in the concentration of carbon-containing gases and hydrogen sulfide in the products. An increase in the amount of water acts oppositely. At the same time, an increase in the temperature and an increase in the amount of water promotes the occurrence of a secondary reaction

$$C_nH_{2n+2} + 2nH_2O \rightarrow nCO_2 + (3n+1)H_2, \quad (4)$$

owing to which an increase in the indicated parameters increases the content in the gas of carbon monoxide and dioxide and decreases the content of unsaturates.

The values of the activation energy are: for the first stage of the reaction in which the demethylation of 2-methylthiophene to thiophene predominates, 9750 cal/mole; for the stage occurring at constant rate where, we assume, the desulfurization of methylthiophene takes place on Ni or Co sulfide, 21,200 cal/mole; these values are close to the literature values.

This reaction of dealkylation of methylthiophene is a model reaction for the production of thiophene from its alkyl derivatives; therefore, the present work shows that it is possible in principle to obtain the raw material for syntheses based on thiophene from sulfur-containing petroleum and shale oils [12]. In view of the fact that the desired reaction proceeds in the first part of the curve (see Fig. 1), the process can be carried out in a moving bed with continuous regeneration of the catalyst.

## EXPERIMENTAL

The experiments were carried out in a catalytic apparatus, including a reactor, which was previously described [13]. The catalysts used in the work had the compositions $Ni/Al_2O_3$ 1 : 1 and 1 : 2, and $Co/Al_2O_3$ 1 : 1, and were prepared by the method of Zelinskii [14]. The catalyst was reduced before an experiment for an hour at the temperature of the experiment, and was held in the manner described in reference [9] during non-operating periods.

The starting materials – thiophene and 2-methylthiophene – were purified by the formation and subsequent decomposition of their mercury acetates [15].

The materials had the following constants. Thiophene: $d_4^{20}$ 1.0640, $n_D^{20}$ 1.5275, b. p. 82-83°/744 mm; 2-methylthiophene: $d_4^{20}$ 1.0200, $n_D^{20}$ 1.5190 b. p. 110-111°/752 mm (the literature values are, respectively: $d_4^{20}$ 1.0644 and 1.0194, $n_D^{20}$ 1.5287 and 1.5203, b. p. 84.12°/760 mm and 112.5°/760 mm).

The 2-methylthiophene and water were charged to the apparatus at constant rates of 0.078 ml/minute for the organic material and 0.70 ml/minute ($\omega$ = 48) and 2.70 ml/minute ($\omega$ = 177) for the water.

The gas was collected and its rate of production measured with a UGSP gas holder. The gas was analyzed in a VTI apparatus. The hydrogen sulfide was absorbed with an acid solution of cadmium chloride [16]. The percent of saturated hydrocarbons was calculated on the assumption that the major part of the saturated hydrocarbons was pentane.

TABLE 3

| Expt. No. | Catalyst | Regeneration time (hours) | ω | Temperature (°C) | Thiophene content after the first 6 minutes of the expt. (%) |
|---|---|---|---|---|---|
| 57 | $Ni/Al_2O_3$ (1 : 1) After use | 0.5 | 48 | 250 | 49 |
| 58 | | 1.0 | 48 | 250 | 56 |
| 59 | | 2.0 | 48 | 250 | 65 |

The content of thiophene and 2-methylthiophene was determined from the absorption spectra of aqueous solutions in the ultraviolet region.

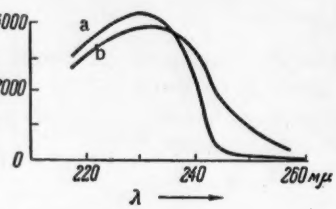


Fig. 2. Absorption curves for aqueous solutions of thiophene (a) and 2-methylthiophene (b).

Although literature data are available on the ultraviolet spectra of thiophene derivatives [17], it has been recommended that analyses of small quantities of them be carried out by the more significant infrared spectra [18] or by color reactions with cerium nitrate (it has been indicated that the method can be used only for the qualitative determination of mixtures [19]).

We took the ultraviolet absorption spectra of aqueous solutions of thiophene, 2-methylthiophene, and their mixtures of various compositions. The absorption maxima found, 230 mμ for thiophene and 234 mμ for methylthiophene (see Fig. 2), agree with the literature values [17]. We were able to show that Lambert-Beer's law applied to this solution and that the method could be used for the determination of the concentrations of thiophene and 2-methylthiophene in their mixtures. In view of the sloping form of the curves and the close location of the maxima, the absolute error was ± 5% (see Table 4). The data in Tables 2, 3, and 4 are average values for a number of determinations.

TABLE 4

| | Thiophene content (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| Actual | 8.3 | 15.4 | 30.1 | 41.7 | 10.6 | 10.6 | 30.1 |
| From the spectra | 11.9 | 9.9 | 25.2 | 38.0 | 6.1 | 7.3 | 33.3 |
| Absolute error | +3.6 | −5.5 | −4.9 | −3.7 | −4.5 | −3.3 | +2.9 |

The combined catalyzates from several experiments in which thiophene was formed were separated, the organic layer was dried and purified by the formation and decomposition of the mercury acetate, and was then distilled from a small flask with a dephlegmator (2 ml). The purified product had the following constants: experiments 62-64: $d_4^{20}$ 1.0215, $n_D^{20}$ 1.5210, i. b. p. 65°, 10% point 109°; experiment 65: $d_4^{20}$ 1.0210, $n_D^{20}$ 1.5205, i. p. b. 72°, 20% point 109°.

## LITERATURE CITED


[1] T. A. Slovokhotova, Bull. Moscow State Univ. No. 8, 67 (1949).

[2] A. A. Balandin, T. A. Slovokhotova and I. A. Strashnova, Bull. Moscow State Univ., No. 1, 101 (1957).

[3] T. A. Slovokhotova, L. I. Sovalova, B. A. Kazanskii and A. A. Balandin, Bull. Moscow State Univ. No. 10, 65 (1954).

[4] A. A. Balandin, L. I. Sovalova and T. A. Solokhotova, Proc. Acad. Sci. USSR, 110,79 (1956).*

[5] T. A. Solokhotova, Candidates Dissertation, Moscow State Univ., 1948.

[6] W. F. Faragher, J. C. Morell and S. Comay, Ind. and Eng. Chem. 20 (1928).

[7] J. E. Elgin, G. H. Wilder and H. S. Taylor, Ind. and Eng. Chem. 527, 22, 1284 (1930).

[8] N. A. Orlov and A. S. Broun, Chem. Solid Fuels, 3, 817 (1932).**

[9] B. Kubota and K. Joshikawa, Japan, J. Chem. 2, 45 (1925); Chem. Abstr. 20, 860 (1926).

[10] B. L. Moldavskii and Z. I. Kumari, J. Gen. Chem. 4, 298 (1934).

[11] B. L. Moldavskii and N. Prokopchuk, J. Appl. Chem. 5, 619 (1932).

[12] Ia. L. Gol'dfarb and I. S. Korsakova, Proc. Acad. Sci. USSR, 96, 283 (1954); Ia. L. Gol'dfarb and B. P. Fabrichnyi, Proc. Acad. Sci. USSR, 100, 461 (1955); Ia. L. Gol'dfarb and M. B. Ibragimova, Proc. Acad. Sci. USSR, 106, 469 (1956).

[13] A. P. Rudenko and T. A. Solokhotova, Factory Labs. No. 1, 121 (1955).*

[14] N. D. Zelinskii, Coll. Works, 3, Moscow, 1955, p. 73.

[15] W. Steinkopf, Die Chemie des Tiophens, 1941, S. 401.

[16] E. H. M. Badger, R. H. Griffith and W. B. S. Newling, Proc. Roy. Soc. London, A, 197, 184 (1949).

[17] H. D. Hartough, Thiophene and its Derivatives, N. J. — London, 1952.

[18] J. Wender, R. Levine and M. Orchin, J. Am. Chem. Soc. 72, 4375 (1950).

[19] H. D. Hartough, Anal. Chem. 20, 860 (1948).

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* Original Russian pagination. See C. B. Translation.

** In Russian.

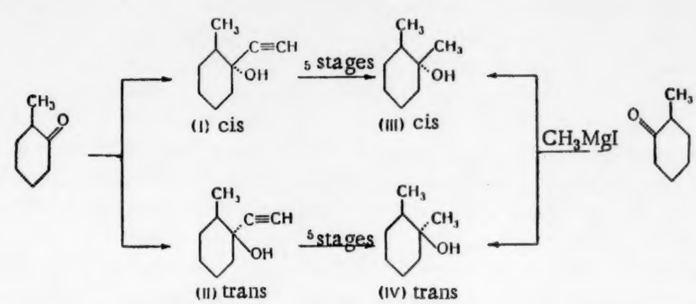
OPTICAL INVESTIGATION OF THE CONFORMATIONS OF SOME GEM-SUBSTITUTED CYCLOHEXANES

M. I. Batuev, A. A. Arkhem, A. D. Matveeva, A. V. Kamernitskii and Academician I. N. Nazarov

The physical properties and reactivity of a functional group depends on its position* — axial or equatorial — in the conformation.

It is sometimes possible to establish this position by chemical means, but frequently this can be accomplished only by a physical method of investigation [1, 2].

In the present work, we made an effort to determine by an optical method the conformations of the epimeric 2-methyl-1-ethynylcyclohexanols (I) and (II) and 1,2-dimethylcyclohexanols (III) and (IV), which we had previously synthesized [3]. The liquid mixture of acetylenic alcohols (I) and (II), obtained from ortho-methylcyclohexanone by Favorskii reaction, were separated into the isomers by means of prolonged freezing out of the cis-isomer (I) and subsequent crystallization of it. The liquid trans-isomer (II) resulting from the separation contained approximately 10% of isomer (I) as an impurity. The mixture of alcohols (III) and (IV), prepared by the interaction of ortho-methylcyclohexanone with methylmagnesium iodide, was separated by distillation in a column equivalent to 40 theoretical plates. The constants of the cis-trans-isomers (III) and (IV) agreed with the literature values [4]. Chiurdoglu [4] first identified the cis- and trans-forms (III) and (IV) of 1,2-dimethylcyclohexanol by means of the Auwers-Skita rule, the rule of trans-elimination of water, and the hydrogenolysis rule, which was discovered by him. The acetylenic alcohols (I) and (II) were previously converted by us to the known pair of cis- and trans-carbinols (III) and (IV) without disturbing the asymmetric center [3].




The physical properties of compounds (I) — (IV) are presented in Table 1.

Raman spectra of these compounds in the liquid phase were taken with an ISP-51 spectrograph with a medium-speed camera using the blue line at 4358 A from a mercury lamp for excitation: **

*In this paper, conformations are determined by the relative position of the largest substituents, in the case cited — methyl and ethyl groups.

**Intensity notation: b) broad line, s) sharp line, db) doublet; asterisks denote lines in the background which are common with neighboring lines marked with the same number of asterisks. The spectra of (III) and (IV) have been published in reference [5] but in incomplete form, ending in the frequency region of $\sim 1450\ cm^{-1}$.

(I) cis-2-methyl-1-ethynylcyclohexanol, Δν см$^{-1}$: 82 (2), 92 (2), 114 (3*), 124 (3*), 153(6**) 166 (3**), 179 (3**), 212 (2), 222 (4), 231 (4), 240 (1), 258 (1), 289 (1), 301 (0), 323 (3*), 332 (3*), 358 (1), 373 (1), 387 (1), 402 (3), 442 (2*s), 450 (2*p), 473 (4 db), 490 (0), 526 (2*), 540 (1*), 593 (3), 624 (1s), 637 (1s), 649 (1*), 661 (8*), 691 (1), 704 (1), 804 (2), 838 (3), 863 (2), 888 (1), 908 (1), 928 (1), 963 (0), 985 (4*), 997 (4*), 1057 (4*), 1067 (4*), 1090 (1), 1114 (4*),

1127 (2*), 1155 (4**), 1166 (4**), 1195 (1), 1212 (2), 1225 (1), 1251 (1), 1266 (4 db), 1295(1), 1332 (2*), 1346 (2*), 1358 (2*), 1447 (6**), 1456 (1**), 1467 (3**), 2090 (1), 2101 (6 b, db), 2118 (1), 2851 (6), 2864 (4), 2893 (3*), 2909 (3*), 2922 (4*), 2933 (8*), 2945 (8*), 2957 (2*), 2969 (2*), 2984 (1*), 3269 (1**), 3283 (1**), 3293 (3**), 3315 (1**), 3350—3600 (1, band ), 3585 (1), 3600 (3), 3615 (1), 3631 (1), 3654 (1).

(II) trans-2-methyl-1-ethynylcyclohexanol, Δν см$^{-1}$: 78 (2*), 92 (2*), 116 (2**), 126 (2**), 152 (5 b*), 182 (3*), 214 (3**), 227 (3**), 264 (0), 288 (0), 315 (0*), 333 (3*), 338 (0*), 362 (0), 380 (0), 398 (4), 421 (0), 448 (0), 468 (4), 489 (3), 530 (3), 553 (3), 592 (3), 649 (3), 660 (4), 696 (7*), 705 (2*), 806 (3p), 833 (4), 864 (3p), 896 (1), 925 (1), 967 (2*s), 983 (3*s), 996 (4*s), 1033 (1), 1056 (4*), 1064 (4*), 1114 (3**), 1129 (3**), 1153 (4*), 1168 (4*), 1194 (2**), 1213 (2**), 1230 (2**), 1248 (1*), 1263 (4*), 1268 (1*), 1302 (2 db), 1329 (3*), 1346 (4*db), 1447 (8**), 1459 (4**), 1463 (4**), 2093 (1*), 2105 (9*b, db), 2118 (1*), 2655 (1 b**). 2684 (1** b), 2735 (3), 2809 (1), 2854 (6*), 2903 (2*), 2919 (2*), 2930 (10*), 2942 (10*), 2970 (4*), 2983 (2*), 3268 (1**), 3283 (1**), 3298 (1**), 3314 (3**), 3350—3614 (1 band ), 3581 (1), 3593 (1), 3614 (3,) 3629 (1), 3653 (1).

III cis-1,2-dimethylcyclohexanol, Δν см$^{-1}$: 245 (0), 273 (3*), 291 (3*), 328 (3), 368 (4*), 387 (4*), 444 (4), 484 (1), 524 (6), 566 (3), 603 (3), 622 (1), 695 (10), 803 (3), 835 (5), 857 (5), 888 (4), 915 (4), 939 (4*), 951 (6*), 980 (4s) 988 (6), 1014 (5), 1064 (5), 1092 (5), 1153 (4*), 1170 (6), 1189 (1*), 1214 (0), 1237 (3), 1262 (7*b), 1275 (2*), 1304 (2), 1335 (4*), 1350 (4*), 1369 (0), 1409 (0), 1441 (9*), 1457 (4*), 1471 (2*), 2629 0), 2659 (0), 2720 (0), 2857 (6*), 2895 (2*), 2914 (4*), 2928 (10*), 2943 (10*), 2970 (4*), 2985 (4*), 3330—3500 (2, band ), 3580 (1), 3606 (4), 3619 (1), 3639 (1), 3652 (1).

(IV) trans-1,2-dimethylcyclohexanol Δν см$^{-1}$: 204 (0 b), 230 (0 b), 330 (0 b), 369 (1 b), 442 (4 db), 468 (0 db), 497 (3), 519 (0), 536 (0), 556 (5), 580 (0), 617 (0), 658 (0), 673 (0), 698 (10), 765 (0), 798 (3), 829 (4), 857 (5), 888 (3), 909 (3), 944 (6), 969 (0), 988 (3*), 1007 (6*), 1039 (0), 1061 (3), 1088 (5), 1109 (1s), 1122 (1s), 1139 (1s), 1154 (1s, 1175 (6), 1215 (1*), 1234 (3*), 1263 (5**), 1277 (5**), 1303 (2 b, db), 1331 (3*), 1347 (3*), 1358 (3*), 1435 (1*), 1449 (6**), 1465 (3**), 2664 (0), 2728 (0), 2853 (6*), 2871 (5*), 2899 (4*), 2923 (10*), 2936 (10*), 2965 (4*). 2982 (3*), 3380—3530 (2, band ), 3582 (1), 3608 (1), 3619 (4), 3636 (1), 3659 (1).

Spectra were also taken of the first two compounds in 10% solution in carbon tetrachloride.

In the Raman spectra of each of the two acetylenic alcohols (I) and (II) and their carbon tetrachloride solutions, not one, but three or four characteristic frequencies were observed for the pulse vibration of the ring and for the vibrations of the C≡C, C−H in −C≡C−H, and O−H bonds (in the monomers) (see Table 2). Moreover, in the spectra of the cis-isomer (I) and its carbon tetrachloride solution, for each of the indicated characteristic bonds one line was distinguished by its greater intensity; these lines were also present in the spectra of the trans-isomer, but with a weak intensity. And, on the contrary, the most intense of these characteristic frequencies in the spectra of trans-isomer (II) and its carbon tetrachloride solution were also present in the spectra of the cis-isomer (I). This indicates the presence as an impurity of the predominant conformation of one isomer in the other (especially I in II, see above). The presence of other weak lines in the regions of the above-mentioned characteristic frequencies in the spectra of both I and II and their solutions in carbon tetrachloride (see Table 2) indicates the presence of very small amounts of other conformations (possibly even the boat form) in the mixtures containing the predominant conformations. The mixture of conformations in I and II is indicated by the greater number of observed lines in their spectra in comparison with the theoretical number expected for the presence of only one conformation in these substances (even without taking into account degeneracy of vibrations. Let us proceed to a clarification of the predominant conformations in (I) and (II), which are characterized by the most intense vibrational frequencies of the characteristic bonds.

That the frequency of the pulse vibration of the ring of isomer (I), 661 cm$^{-1}$, is lower than that of isomer (II), 696 cm$^{-1}$, confirms [1] that isomer I) is actually the cis-, and isomer (II) is actually the trans-form of 2-methyl-1-ethynylcyclohexanol. The conformations of these compounds can be determined from the other vibrational frequencies presented for the characteristic bonds. The intense vibrational frequencies of the C≡C bonds in the spectra of the liquid cis- and trans-isomers (I) and (II) appear fused, but they are separated in the spectra of the solutions, the frequency of the C≡C bond in (I) (2100 cm$^{-1}$) being lower than in (II) (2108 cm$^{-1}$)

## TABLE 1

Physical Properties of the 2-Methyl-1-ethynylcyclohexanols (I) and (II) and of the 1,2-Dimethylcyclohexanols (III) and (IV)

| Compound | M. p., °C | B. p., °C/mm Hg | $n_D^{20}$ |
|---|---|---|---|
| (I) cis-2-Methyl-1-ethynylcyclohexanol | 56—57 | 75/10 | 1.4780 |
| (II) trans-2-methyl-1-ethynylcyclohexanol | (liquid) | 69—70/10 | 1.4770 |
| (III) cis-1,2-dimethylcyclohexanol | 23.5—24 | 74,5/15,5 | 1.4665 |
| (IV) trans-1,2-dimethylcyclohexanol | 11.5—13 | 61/13 | 1.4639 |

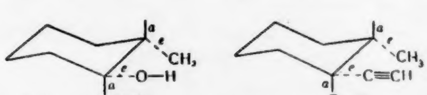
## TABLE 2

Vibrational Frequencies of the Characteristic Bonds of cis- and trans-2-Methyl-1-ethynylcyclohexanols *

| Compound | Pulse vibration frequency of the ring | C≡C | C—H B—C≡CH | O—H (monomer) |
|---|---|---|---|---|
| (I) cis-2-Methyl-1-ethynylcyclohexanol | 649 (1) | — | 3269 (1) | 3585 (1) |
| | 661 (8) | 2090 (1) | 3283 (1) | 3600 (3) |
| | 691 (1) | 2101 (b, db) | 3293 (3) | 3615 (1) |
| | 704 (1) | 2118 (1) | 3315 (1) | 3631 (1) |
| | — | — | — | 3654 (1) |
| 10%(I) + $CCl_4$ | 648 (1) | 2091 (1) | 3270 (1) | 3585 (1) |
| | 660 (3) | 2100 (4) | 3285 (1) | 3603 (3) |
| | 688 (1) | 2110 (2) | 3293 (3) | 3615 (1) |
| | 703 (1) | 2121 (1) | 3317 (1) | 3634 (1) |
| | — | — | — | 3654 (1) |
| (II) trans-2-Methyl-1-ethynylcyclohexanol | 649 (3) | — | 3268 (1) | 3581 (1) |
| | 660 (4) | 2093 (1) | 3283 (1) | 3593 (1) |
| | 696 (7) | 2105 (9b, db) | 3298 (1) | 3614 (3) |
| | 705 (1) | 2118 (1) | 3314 (3) | 3629 (1) |
| | — | — | — | 3653 (1) |
| 10% (II) + $CCl_4$ | 651 (1) | 2092 (1) | 3270 (1) | 3580 (1) |
| | 662 (0) | 2099 (2) | 3283 (1) | 3599 (1) |
| | 695 (4) | 2108 (4) | 3298 (1) | 3614 (1) |
| | 706 (2) | 2122 (1) | 3314 (3) | 3630 (3) |
| | — | — | — | 3651 (1) |

* The intensities of the lines of the pure substances and their solutions are not comparable, since the spectra of the solutions were taken with a considerably greater exposure; the relative intensity of a line within the bounds of a given spectrum has significance. The vibrational frequencies of the O—H bonds are those of the hydroxyl groups of the molecules, which, apparently, are not associated through hydrogen bonding; a broad band shifted toward the lower frequencies is characteristic for the O—H bonds in the latter (see above spectra).

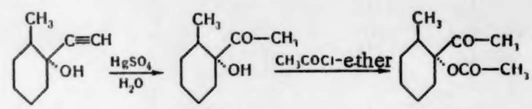
Analogously, the vibrational frequencies of the C—H in —C≡CH (3293 $cm^{-1}$) and O—H (3600 $cm^{-1}$) bonds in (I) are lower than for these bonds in (II) (respectively, 3314 and 3614 $cm^{-1}$). According to [1], this means that the predominant conformation in the cis-isomer (I) is ae, and that in the trans-isomer (II) is ee:



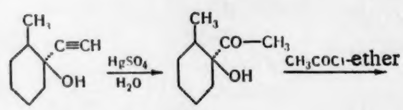

(I) ae (II) ee

In the ae conformation, the influence of the ring on the hydroxyl group, which is in an equatorial position, is more significant than in conformation ee in which it is in an axial position. In the ae conformation, the equatorial hydroxyl group is more protonized, and in this connection it has a lower vibrational frequency (3600 $cm^{-1}$), a lower bond energy, and a greater interatomic distance; i.e., it has more acidic properties than the axial hydroxyl group in the ee conformation. On the other hand, $C \equiv C$, $C-H$, and $-C \equiv CH$ bonds in an equatorial position, in which they occur in the ee conformation, are more electronized; i.e., they have higher vibrational frequencies, higher bond energies, and smaller interatomic distances than in the axial position in conformation ae [1, 6]. In the isomeric 1,2-dimethylcyclohexanes, the pulse frequency of the ring, though insignificantly, is nevertheless lower in (III) (695 $cm^{-1}$) than in (IV) (698 $cm^{-1}$). This indicates that (III) is the cis- and (IV) is the trans-isomer [1]. In addition, the lower vibrational frequency (3608 $cm^{-1}$) of the hydroxyl group in (III) (monomer) as compared to its frequency in (IV) (2618 $cm^{-1}$) indicates that the hydroxyl group in isomer (III) occupies an equatorial position and that the latter compound exists in the ae conformation. In isomer (IV), on the contrary, the hydroxyl group occupies an axial position, and isomer (IV) exists in the ee conformation. The presence of other, weak-intensity frequencies in the region of the vibrational frequencies of the hydroxyl group of the monomeric molecules indicates that in forms (III) and (IV) there apparently are other conformations, which are present in very small amounts.

A relation between reactivity and conformation in a number of cyclohexane derivatives has recently been observed by us [7]. In this case, it was shown that the cis-α-ketol (V) prepared from (I) and having a more acidic, equatorial hydroxyl group, acetylates under milder conditions than the trans-α-ketol prepared from (II) and having an axially located hydroxyl, which does not acetylate under these conditions, but tends toward dehydration.




(I) (V)




(II) (VI)

## LITERATURE CITED


[1] M. I. Batuev, A. A. Arkhem, A. D. Matveeva and I. N. Nazarov, Proc. Acad. Sci. USSR, 117, 423 (1957). *

[2] C. Carlisle and Y. Crowfoot, Proc. Roy. Soc. A, 184, 64 (1945).

[3] I. N. Nazarov, A. A. Arkhem and A. V. Kamernitskii, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1958,** 631; I. N. Nazarov, A. V. Kamernitskii and A. A. Arkhem, J. Gen. Chem. 28, No. 6 (1958).**

[4] G. Chiurdoglu, Bull. Soc. Chim. Belg. 47, 241 (1938); 50, 8 (1941); 50, 31 (1941).

[5] G. Chiurdoglu and A. Guillemonat, Bull. Soc. Chim. France, 5, 1328 (1938).

[6] M. I. Batuev, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956,* 1329; J. Gen. Chem. 26, 1888 (1956);** 27, 876 (1957).**

[7] I. N. Nazarov and A. A. Arkhem, J. Gen. Chem. 28, No. 6 (1958);* J. Pasqual, J. Sistare, A. Regas, J. Chem. Soc. 1949, 1943.


* We note, in passing, errors in [1]. On page 424: in the scheme after the e line from the top, on the left side of the first series of formulas insert the figure "I", and on the left side of the second series of formulas insert the figure "II"; between the first and second formulas in both the first and second series of formulas the arrows should be reversed to the left; in the scheme on page 423, in place of the designation "(p)", insert "(a)"; on page 426, line 13 and in the scheme, "ep" should be replaced by "ea".

** Original Russian pagination. See C. B. Translation.


Institute of Fossil Fuels Academy of Sciences USSR
Institute of Organic Chemistry Academy of Sciences



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## THE CAGE EFFECT AND THE THERMAL STABILITY OF POLYMERS

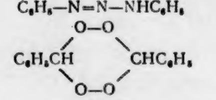
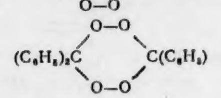
B. A. Dolgoplosk, B. L. Erusalimskii, E. B. Milovskaia and
G. P. Belonovskaia

(Presented by Academician B. A. Kargin, January 6, 1958)

There exists a large number of organic substances whose thermal stability in solution or in the melt is considerably lower than in the solid state. The various compounds containing labile bonds (peroxides, azo, and diazo compounds) are the most typical in this respect, the decomposition of these compounds beginning at their melting points. Furthermore, thermal decomposition of these substances in solution proceeds at a significant rate at a much lower temperature (see Table 1).

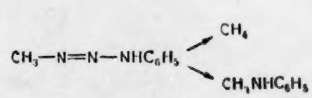
TABLE 1

Thermal Stability of Certain Compounds in the Solid State and in Solution

| | | M. p., °C | Thermal decompn. temp. in soln., °C | Source |
|---|---|---|---|---|
| Azobisisobutyronitrile | $(CH_3)_2-C(CN)-N{=}N-C(CN)(CH_3)_2$ | 104 with decomposition | 70—80 | (1) |
| Benzoyl peroxide | $C_6H_5-COOC-C_6H_5$ (with O on each C) | 103.5 " | 60—70 | (2) |
| Paranitrobenzoyl peroxide | $n-NO_2C_6H_4COOOCC_6H_4NO_2$ (with O on each C) | 156 " " | 80 | (3) |
| 4,4'-bis(benzenediazoamino)biphenyl | $C_6H_4-N{=}N-NHC_6H_5$ / $C_6H_4-N{=}N-NHC_6H_5$ | 180 " " | 135 | Our data [4] |
| Benzaldehyde diperoxide |  | 200 " " | No data | |
| Benzophenone diperoxide |  | 212.5 " " | No data | |

It seems to us that the experimental data presented below permit connecting this phenomenon with the greater role played by the cage effect (primary recombination of free radicals) in viscous and solid media.

As has been shown previously, the thermal decomposition of methylphenyltriazene in a hydrocarbon medium leads to the formation of methane and methylaniline [5]:



It is most probable that the methylaniline is formed as a result of the recombination of radicals formed at the instant of decomposition in the "cage." This follows from the fact that the yield of alkylanilines during the decomposition of various alkylaryltriazines is practically independent of the activity of the alkyl free radicals formed as a result of the decomposition of the triazenes [5]. Moreover, the formation of methylaniline through recombination acts outside the cage does not appear possible owing to the high activity of the methyl radical in reactions with isopropylbenzene.

TABLE 2

Yield of Basic Products from the Conversion of Free Radicals During the Decomposition of Methylphenyltriazene in Various Media. Triazene Concentration, 10%. Temperature, 100°

| Content of polymer in isopropylbenzene, wt. % | | Yield, % of theoretical | |
|---|---|---|---|
| | | $CH_4$ | $CH_3NHC_6H_5$ |
| – | – | 49.0 | 15.0 |
| 5 | – | 47.5 | |
| 50 | – | 35.5 | |
| 66 | – | 27.0 | Not determined |
| – | 5 | 45.0 | |
| – | 50 | 28.0 | |
| – | 90 | 9.5 | 43.5 |

TABLE 3

Effect of Polymer Molecular Weight on Methane Yield During the Decomposition of Methylphenyltriazene

| Content of polystyrene in isopropylbenzene, wt. % | Polymer molecular weight | Yield of $CH_4$, % of theoretical |
|---|---|---|
| 66 | 600,000 | 20 |
| 66 | 600,000 | 20 |

We have established that during the decomposition of methylphenyltriazene in hydrocarbon–polymer systems, the yield of methane decreases with an increase in the viscosity of the medium. Simultaneously, as was shown in the polystyrene–cumene system, there is an increase in the yield of primary recombination product, namely, methylaniline (see Table 2).

The conclusion that the decrease in the yield of methane is connected with the increase in viscosity, and not with the decrease in the amount of isopropylbenzene, is confirmed by the following data. We showed that at equal weight-concentrations of the different samples of polystyrene in isopropylbenzene, the methane yield was lower the higher the molecular weight of the polymer (see Table 3).

The data presented indicate the essential influence of viscosity of the medium on the effectiveness with which interaction in the cage proceeds. The results of our work permit consideration of the question of the possible influence of the aggregate state on the thermal stability of substances containing labile bonds (see Table 1) and also of polymers possessing a high softening temperature. The difference in the behavior of compounds of similar nature in the solid state and in solution (or in the melt) can be explained specifically by the considerable role played by the cage effect in the solid state. A consideration of the facts touching on the thermal stability of high-melting polymers makes this conclusion particularly convincing.

As is well known, polyparaxylene, $\sim CH_2C_6H_4CH_2CH_2C_6H_4CH_2 \sim$, the melting point of which amounts to 425°, decomposes only after transition into the molten state. In solution, this polymer undergoes considerable decomposition at temperatures as low as 302° [6]. There exist a number of other polymers, possessing high melting points, which are stable until the melting point is reached, for example:

$$\sim CH_2CH_2O\underset{\underset{O}{\|}}{C}C_6H_4C = CC_6H_4\underset{\underset{O}{\|}}{C}OCH_2CH_2 \sim$$

M. p. 420° (with decomposition)

$$\sim NH\,(CH_2)_6\,NH\,COC_6H_4CO \sim$$

M. p. 350° (with decomposition)

Obviously, we are here dealing with "superheated" polymers which begin to undergo decomposition only after transition through the glass temperature, when the viscosity of the system sharply decreases. It can be assumed that in rigid systems (below $T_g$ or below the melting point for crystalline polymers), the primary thermal acts of C—C bond rupture do not cause depolymerization precisely because of the cage effect, which returns the system to the initial state. Only a transition into the elastic region creates conditions for the destruction process, which appears as a sharp decrease in the thermal stability of the polymers above their softening or melting points.

On the basis of the above considerations, it can be assumed that the thermal stability of polymers characterized by a high melting point must undergo sharp discontinuities during the transition from the rigid state into the elastic and from the elastic state into solution.

In the latter case, the thermal stability of the polymer is determined by the strength of the skeletal bonds of the polymer chain. The above-mentioned fact, indicating a decrease in the thermal stability of polyparaxylene in solution, supports this point of view.

On the basis of these concepts, it can be concluded that the problem of the increase in thermal stability of carbon-chain polymers in the glass state first of all boils down to the requirement for an increase in the melting point. For rubber-like polymers, in which the cage effect appears to a lesser extent, high thermal stability can apparently be attained only at the expense of the strength of the skeletal bonds of the main chain.

## LITERATURE CITED


[1] C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, J. Am. Chem. Soc. 71, 2661 (1949).

[2] P. D. Bartlett and K. Nozaki, J. Am. Chem. Soc. 68, 1686 (1946).

[3] Synthesis of Organic Compounds [Organic Syntheses], 3, Foreign Lit. Press, 1952, p. 377 (Translation).

[4] C. Marvel and N. Nichols, J. Org. Chem. 6, 296 (1941).

[5] B. A. Dolgoplosk, B. L. Erusalimskii, V. A. Krol' and L. M. Romanov, J. Gen. Chem. 24, 1775 (1954).*

[6] L. Auspos and C. Burnam, et al., J. Pol. Sci. 15, 19 (1955).

[7] R. Hill, Fibres from Synthetic Polymers, Amsterdam, 1953, p. 317.

[8] J. Butler, D. McGowan and W. Toland, U. S. Patent 2,657,195; 1953, Chem. Abstr. 48, 1019 (1954).



Institute of High-Molecular Compounds
Academy of Sciences USSR



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* Original Russian pagination. See C. B. Translation.

# A NEW METHOD FOR THE PREPARATION OF HYDROXYALKYLPHOSPHONIC ACIDS

V. K. Kuskov, G. F. Bebikh and A. D. Iaroshenko

(Presented by Academician S. I. Vol'fkovich, November 5, 1957)

In investigating esters of boric acid, we found that they do not react with phosphorus trichloride, even on boiling. Phosphoryl chloride readily decomposes boric acid esters when the mixture is heated on a water bath, the reaction proceeding according to the equation:

$$(AlkO)_3B + POCl_3 \text{ — } BPO_4 + 3AlkCl.$$

This reaction goes very slowly at 0°. Hydrogen chloride does not react with borates prepared from primary and secondary alcohols.[1]. Therefore, we surmised that boric acid esters quite possibly could be phosphorylated by the reaction of Soborovsky, Zinov'ev and Englin [2]:

$$RH + PCl_3 + 0.5O_2 \text{ — } RPOCl_2 + HCl.$$

This reaction was first proposed for the phosphorylation of hydrocarbons, and was later extended to alkyl halides, ethers, and certain other compounds.

In the present work, we found that esters of boric acid (prepared from the appropriate alcohols as in [3]) readily enter into this reaction. The reaction proceeds effectively only if the reaction mixture is well cooled. Without this cooling, the phosphorus trichloride is simply oxidized to the oxychloride, and few phosphorylation products or none at all are obtained. The phosphorylation reaction was first studied using tributyl borate and triisobutyl borate. The reaction can be represented schematically in the form:

$$(C_4H_9O)_3B + PCl_3 \text{ — } 0.5O_2 \text{ — } (C_4H_9O)_2BOC_4H_8POCl_2 + HCl.$$

In the best variant, 4 moles of phosphorus trichloride are used per mole of tributyl borate. Obviously, more than one butyl group of the tributyl borate is phosphorylated, since the yield of hydroxybutylphosphonic acid is 60%, if it is assumed that it is theoretically possible to obtain 3 moles of hydroxybutylphosphonic acid per mole of tributyl borate. The phosphorylated boric acid esters proved to be unstable compounds. During an attempt to distill the phosphoryl chloride obtained during the phosphorylation of triisobutyl borate, a violent reaction began at about 80-100°, and the reaction mass congealed into a solid, colorless resin. Distillation under vacuum at 15 mm gave phosphoryl chloride and a mixture of acid chlorides, including $C_4H_9OPOCl_2$. The residue – a thick, slightly colored mass – had chlorine and phosphorus contents close to those required by $B(OC_4H_8POCl_2)_3$, but the molecular weight was about 300 (323 and 315 in two determinations) instead of the calculated 578. Evidently, some cleavage occurred. In order to separate and purify the hydroxyphosphonic acids, at the conclusion of the phosphorylation, the reaction products were poured into ice water and were then evaporated several times to remove hydrochloric and boric acids. Further, the phosphoric acid was separated as the magnesium ammonium salt in accordance with the method proposed by Page [4], and the corresponding hydroxyalkylphosphonic acid was precipitated from the filtrate as the lead salt. Decomposition of the lead salt with hydrogen sulfide gave the free hydroxyphosphonic acid.

α-Hydroxyphosphonic acids were prepared by phosphorylation of trimethyl borate and tribenzyl borate. These acids had been prepared previously [4, 5] from the corresponding aldehydes. The analytical data agreed with those in the literature. Crystalline hydroxybutylphosphonic acid was obtained by phosphorylation of butyl borate, and this, in distinction from the α-hydroxybutylphosphonic acid described in the literature, did not form the acid chloride when treated with phosphorus pentachloride, but did react vigorously with the formation of a white, solid product which was evidently a polycondensation product. From triethyl borate, we were able to obtain hydroxyethylphosphonic acid in the form of the impure lead salt; it contained phosphoric acid, although the phosphoric acid impurity was first separated as the magnesium ammonium salt. Evidently, the product was the salt of the unstable β-hydroxyethylphosphonic acid, which, similarly to its previously prepared ester [6], readily cleaved with the formation of phosphoric acid. The other hydroxyalkylphosphonic acids were isolated in the form of lead salt; the free acids were not crystalline and, possibly, were mixtures of isomers. On heating of the phosphoryl chlorides of the boric esters of these acids immediately after phosphorylation, they decomposed, and a vigorous reaction occurred accompanied by the evolution of hydrogen chloride.

During the phosphorylation of isobutyl borate, an experiment was carried out on the conversion of the resulting acid chlorides to the ethyl esters by treatment with ethyl alcohol in pyridine, analogously to the method for the preparation of esters of phosphonic acids which was published earlier [7].

The mixture of esters did not distill, and during an attempted distillation under vacuum, even polymerization of the triethyl phosphate occurred. An attempt was also made to prepare the pyrophosphate by the method of Dvornikoff and Morill [8] with the intention of obtaining a pyrophosphate of the following type according to the overall equation:

$$B(OC_4H_8POCl_2)_3 + 3POCl_3 + 12C_2H_5OH \rightarrow$$

$$\rightarrow B(OC_4H_8\overset{\overset{O}{\|}}{\underset{OC_2H_5}{P}}-O-\overset{\overset{O}{\|}}{\underset{OC_2H_5}{P}}-OC_2H_5)_3 + 3C_2H_5Cl + 12HCl.$$

Pyrophosphates were obtained several times; however, they had a molecular weight of 1300-1400 instead of the calculated 963, and were obviously polypyrophosphates.

Tests showed that the resulting esters were very weak insecticides for a typical agricultural pest – the grainery weevil.

## EXPERIMENTAL

The phosphorylation of the boric acid esters was carried out in a three-necked flask fitted with a reflux condenser (which communicated to the atmosphere through a calcium chloride tube), a thermometer, a dropping funnel, and a capillary, through which oxygen from a cylinder was passed after drying with calcium chloride and soda lime.

0.1 mole of the boric acid ester was placed in the flask and cooled with an ice-salt mixture; passage of the oxygen through the capillary was then started, the flow rate being such that it was hardly possible to count the bubbles; the rate was substantially 2-3 liters per hour. 0.4 mole (55 g) of phosphorus trichloride was fed from the dropping funnel over a period of 2-2.5 hours, the rate initially being very slow since the reaction is vigorous and an undesirable temperature rise is possible. The reaction temperatures used for the various esters are presented in Table 1. After all of the phosphorus trichloride had been added, the oxygen flow was continued until the temperature ceased to increase and then for another 30 minutes, after which the process was ended. Without permitting the reaction mixture to be heated, the mixture was poured in a thin stream and with stirring into 1.5 liters of cold water, and the mixture was stirred until solution occurred (hydrolysis). Further, the solution was evaporated on a water bath several times until elimination of the hydrogen chloride was complete (the vapors did not react with congo paper).

The mixture was then diluted to a volume of 200-300 ml, ammonia was added to a weakly alkaline reaction, and the phosphoric acid was precipitated with a 10% solution of magnesium nitrate. After 12 hours, the precipitated magnesium ammonium phosphate was filtered and washed with water.

TABLE 1

| Boric acid ester | Temperature, °C | Leadhydroxyalkylphosphonate g | Leadhydroxyalkylphosphonate % of theoretical | Hydroxyalkylphosphonic acid g | Hydroxyalkylphosphonic acid % of theoretical | Analysis* |
|---|---|---|---|---|---|---|
| Methyl | 0 | 57.2 | 54.4 | 12 | 41.7 | M. p. 85°; [4] 85° found %: P 9.33 $CH_3PO_4Pb$. calculated %: P 9.41 |
| Ethyl | 0 | 17.0 | 17.0 | — | — | found %: P 8.95 $C_2H_5PO_4Pb$. calculated %: P 9.35 |
| Propyl | 0—7 | 43 | 41.6 | — | — | found %: P 8.63 $C_3H_2PO_4Pb$. calculated %: P 8.97 |
| Butyl | 4 | 66.5 | 60.0 | 21 | 51.2 | found %: P 8.48 $C_4H_9PO_4Pb$. calculated %: P 8.65 |
| Isobutyl | 0 | 41 | 37.4 | — | — | found %: P 8.48 $C_4H_9PO_4Pb$. calculated %: P 8.65 |
| Isoamyl | 6—12 | 47 | 37.8 | — | — | found %: P 8.11 $C_5H_{11}PO_4Pb$. calculated %: P 8.30 |
| Secondary octyl (2-octanol) | 5 | 22 | 17.0 | — | — | found %: P 8.46; 8.14 $C_8H_{17}PO_4Pb$. calculated %: P 7.51 |
| Cyclohexyl | 25 | 45 | 39.2 | 31.6 | 29.2 | M. p. 137°. found %: P 7.75, 7.98 $C_6H_{11}PO_4Pb$. calculated %: P 8 05 |
| Benzyl | 0 | 31 | 23.7 | — | — | Aniline salt m. p. 200-201°, lit. value [9] 201-202°. found %: P 7.86; 7.89 $C_7H_7PO_4Pb$. calculated %: P 7,83 |

* All analyses for P content relate to the lead salts of the hydroxyalkylphosphonic acids.

The filtrate and wash waters were combined, and a 20% solution of lead acetate or nitrate was added until precipitation was complete. The lead salt was filtered, washed several times with hot water, and dried in air and, finally, in a drying cabinet at 110-115°. In order to liberate the free hydroxyphosphonic acid, the lead salt, undried, was agitated with 200 ml of water, and the lead was then precipitated as the sulfide by treatment with hydrogen sulfide for 5 hours. The lead sulfide precipitate was filtered and washed with hot water. The filtrate was checked for complete precipitation by passing hydrogen sulfide through it; it was then concentrated on a water bath, and the precipitated hydroxyalkylphosphonic acid was dried in a desiccator over phosphorus pentoxide. The results are presented in Table 1.

## LITERATURE CITED


[1] W. Gerrard and M. F. Lappert, J. Chem. Soc. 1951, 2545; C. R. Kinney, H. T. Tompson and L. C. Cheney, J. Am. Chem. Soc. 57, 2396 (1935).

[2] L. Z. Soborovskii, Iu. M. Zinov'ev and M. A. Englin, Proc. Acad. Sci. USSR, 67, 293 (1949); 73, 333 (1950); W. J. Jenzen and J. O. Clayton, J. Am. Chem. Soc. 70, 3880 (1948).

[3] V. K. Kuskov and V. A. Zhukova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 734.*

[4] H. J. Page, J. Chem. Soc. 101, 423 (1912).

[5] W. Fossec, Monatsh., 7, 20 (1886); M. I. Kabachnik, Prog. Chem. 16, 4, 403 (1937); M. I. Kabachnik and E. S. Shepeleva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, 185.

[6] G. V. Chelintsev and V. K. Kuskov, J. Gen. Chem. 16, 1481 (1946).


* Original Russian pagination. See C. B. Translation.

[7] A. D. F. Toy, J. Am. Chem. Soc. 70, 3882 (1948).

[8] M. N. Dvornikoff and H. L. Morill, Anal. Chem. 20, 935 (1948).

[9] J. B. Conant and A. D. Macdonald, J. Am. Chem. Soc. 42, 2337 (1920).

M. V. Lomonosov Moscow
State University

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# CATALYTIC CYCLIZATION OF n-PENTANE AND n-HEXANE WITH THE FORMATION OF A FIVE-MEMBERED RING

A. L. Liberman, G. V. Loza, Chzhan Min-Nan' and
Academician B. A. Kazanskii

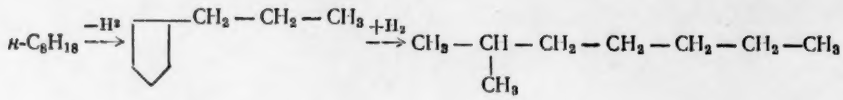
In work published over the past few years, we have shown that paraffinic hydrocarbons cyclize smoothly to homologs of cyclopentane in the presence of platinized carbon [1-5]. Moreover, it was shown that the yield of cyclopentane hydrocarcons depends essentially on the structure of the original paraffinic hydrocarbon. Thus, at 310° and a space rate of 0.2 $hour^{-1}$, the yield of cyclopentane homologs from the reaction over freshly prepared catalyst comprises: 25-35% from isooctane, 12% from 3-ethylpentane, and 3-5% from n-octane. It might be supposed that paraffins of normal structure would cyclize at approximately the same rates, since under somewhat different conditions n-heptane and n-octane give equal yields of cyclization products [1]. Therefore, it was of interest to compare n-octane with n-hexane and n-pentane. The latter hydrocarbon is of particular interest, since thermodynamically it represents an exception of cyclization reactions, yielding a five-membered ring. Indeed, at thermodynamic equilibrium, a mixture of n-pentane and cyclopentane at 500° K and atmospheric pressure contains only 8% cyclopentane, while in equilibrium mixtures of n-hexane, n-heptane, and n-octane with their respective polymethylenes the content of cyclopentane hydrocarbons will comprise 30-40% [3].

Our investigation showed that n-pentane actually does behave differently from the homologs studied, since n-hexane cyclizes similarly to n-octane. Thus, at 310° and a space rate of 0.2 $hours^{-1}$, n-pentane was completely unchanged even over freshly prepared catalyst, while n-hexane was cyclized to the extent of 3.5-4.5%. Moreover, n-pentane did not undergo cyclization even at 330°, and only at 350° did it enter into this reaction; however, at this relatively high temperature the yield of cyclopentane was small. The catalyst was sufficiently active, since isooctane was cyclized to the extent of 30% over a separate portion of this catalyst at 310° and a space rate of 0.2 $hours^{-1}$.

In order to confirm that the expected cyclization products were actually obtained in the cases under consideration, each hydrocarbon was passed over a separate portion of catalyst for a period of several days. The temperature was 350° in the case of n-pentane and 310° for n-hexane; the space rate was the same in each case, namely 0.2 $hours^{-1}$. After determination of their constants and chromatographing, the catalyzates were distilled in efficient columns. Cyclopentane was obtained from the n-pentane catalyzate with a purity of about 99%, judging from its constants. On the basis of Raman data, * the concentrate from the n-hexane catalyzate contained about 95% methylcyclopentane.

It is very curious that, according to Raman data, the overhead fraction from the distillation of the conversion products of the n-pentane conversion contained 25-30% isopentane (1.7% of the total catalyzate). Up to the present time, no reliable proof of the possibility of isomerizing paraffinic hydrocarbons in the presence of platinized carbon has appeared in the literature. It is true that in 1937 Iu. K. Iur'ev and P. Ia. Pavlov [6] reported that n-octane is isomerized into a mixture of isoparaffins when it is passed in a stream of hydrogen over this catalyst, and this work is frequently mentioned in the monograph literature. However, in the light of our work on the cyclization of paraffins to cyclopentanes it might be considered that the isoparaffins obtained by these authors could have been secondary products formed by cyclization of the n-octane and subsequent hydrogenolysis of the cyclopentane hydrocarbons, for example:

*The Raman spectra of the catalyzates were investigated by Kh. E. Sterin, to whom we extend our thanks for this comradely aid.



Since hydrogenolysis of cyclopentane could yield only n-pentane, the appearance of isopentane in the catalyzate is obviously proof of direct isomerization.

## EXPERIMENTAL

Starting materials and catalysts. The n-pentane and n-hexane were prepared by chromatographing the commercial materials and then by distillation in a column with an efficiency of 100 theoretical plates. After distillation, they had the following constants:

| | B. p., °C (760 mm Hg) | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|
| n-Pentane | 36.1 | 1.3575 | 0.6262 |
| n-Hexane | 69.0 | 1.3749 | 0.6594 |

These values are in good agreement with the most reliable literature data [7].

The catalysts consisted of two samples of platinized carbon (20% Pt), prepared as described by N. D. Zelinskii and M. B. Turova-Poliak [8]. In order to compare the activity of the catalysts with the previously used samples, small portions of the catalysts (10 ml) were tested with isooctane at 310° and a space rate of 0.2 hours$^{-1}$. After being chromatographed, the catalyzates had $n_D^{20}$ 1.3975 and 1.3962, which correspond to 30 and 24% yields of 1,1,3-trimethylcyclopentane, respectively. Cyclization of n-pentane was studied with the first of these samples and of n-hexane with the second.

Cyclization of n-pentane. Six experiments of 2-4.5 hours duration were carried out over 60 ml of catalyst. A fresh portion of n-pentane was used each time at 350°, a space rate of 0.2 hours$^{-1}$, and without a carrier gas. The indices of refraction, density, and bromine number were determined for each catalyzate. The catalyzates were then freed of unsaturates by passage through silica gel, after which the indices of refraction and density were again determined. The content of unsaturates was calculated from the bromine number, and the cyclopentane content was calculated assuming additivity of the indices of refraction and of the specific volumes [9], the average of the two resulting values being used. The results of the investigations of the catalyzates before and after chromatographing are presented in Table 1.

The chromatographed catalyzates from all experiments were combined. As a result, there was obtained 107.0 g of catalyzate with $n_D^{20}$ 1.3593, which corresponds approximately to a cyclopentane content of 3.7%. The catalyzate was distilled in a column equivalent to 100 theoretical plates, and the residue from this distillation was distilled in a 35-plate column. The distillation results are collected in Table 2. All the fundamental lines of isopentane were observed in the Raman spectrum of Fraction I; the isopentane content of this fraction was 25-30% or 1.7% based on the total catalyzate. Calculations based on the assumption of additivity of the refractive indices of isopentane and n-pentane led to a closely similar value (2.1%).

The constants of Fraction VII from this distillation were very close to those of cyclopentane. According to the most reliable literature data, this hydrocarbon has the following constants: b. p. 49.262°/760 mm; $n_D^{20}$ 1.4065; $d_4^{20}$0.74538 [7]; aniline point 15.8° [9]. The constants of Fraction VII are still closer to the values calculated for a mixture of 99% cyclopentane and 1% n-pentane: $n_D^{20}$ 1.4061; $d_4^{20}$ 0.7440; aniline point 16.3°.

Cyclization of n-hexane. Nine experiments of 5 hours duration were carried out over 45 ml of catalyst. A fresh portion of n-hexane was used each time at 310°, a space rate of 0.2 hours$^{-1}$, and without a carrier gas. All further treatment of the catalyzates and the determination of their contents of olefins and cyclanes were carried out as in the case of n-pentane. The benzene content of the catalyzate was calculated from the change in the refractive index resulting from chromatographing. The results obtained are presented in Table 3.

TABLE 1

Yields and Properties of n-Pentane Catalyzates

| Expt. No. | n-Pentane fed, g | Properties of catalyzates: before chromatographing: yield, g | $n_D^{20}$ | $d_4^{20}$ | bromine, No. | content of unsaturates, % | after chromatographing: $n_D^{20}$ | $d_4^{20}$ | cyclopentane content,* % |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 28.8 | 28.0 | 1.3612 | 0.6328 | 7.3 | 3.3 | 1.3593 | 0.6312 | 4.2 |
| 2 | 29.4 | 27.0 | 1.3605 | 0.6325 | 9.9 | 4.4 | 1.3592 | 0.6314 | 4.2 |
| 3 | 31.3 | 30.0 | 1.3602 | 0.6307 | 9.0 | 4.0 | 1.3592 | 0.6303 | 3.7 |
| 4 | 12.5 | 11.3 | 1.3604 | 0.6313 | 8.0 | 3.6 | 1.3590 | 0.6301 | 3.3 |
| 5 | 24.1 | 23.8 | 1.3603 | 0.6315 | 9.3 | 4.1 | 1.3592 | 0.6311 | 4.1 |
| 6 | 27.5 | 26.5 | 1.3600 | 0.6302 | 9.5 | 4.2 | 1.3590 | 0.6294 | 3.0 |

*Calculated as the average of the values found from the refractive indices and specific volumes.

TABLE 2

Results of the Distillation of the n-Pentane Catalyzate

| Fraction No. | Boiling range, °C (at 760 mm Hg) | Yield of fraction, % | $n_D^{20}$ | $d_4^{20}$ | Cyclopentane content, % |
|---|---|---|---|---|---|
| I | 29.5—36.1 | 3.9 | 1.3560 | 0.6235 | — |
| II | 36.1 | 4.7 | 1.3575 | 0.6262 | — |
| III | 36.1 | 77.9 | 1.3575 | 0.6262 | — |
| IV | 36.1 | 2.3 | 1.3575 | 0.6262 | — |
| V | 36.1 | 0.9 | 1.3575 | 0.6262 | — |
| VI | 36.1—49.2 | 1.4 | 1.3915 | 0.7071 | 69 |
| VII ** | 49.2 | 2.9 | 1.4063 | 0.7438 | 99 |
| Residue | — | 0.3 | 1.4063 | — | 99 |
| Collected in trap | — | 2.3 | 1.3565 | 0.6248 | — |
| Loss | — | 3.4 | | | |
| | Total | 100.0 | | | |

*Fractions I-IV were distilled in the 100-plate column; the remaining fractions were distilled in the 35-plate column.

**Aniline point of this fraction was 16.0°.

TABLE 3

Yields and Properties of n-Hexane Catalyzates

| Expt. No. | n-Hexane fed, g | Properties of catalyzates: before chromatographing: yield, % | $n_D^{20}$ | $d_4^{20}$ | bromine No. | after chromatographing: $n_D^{20}$ | $d_4^{20}$ | Catalyzate compositions, %: olefins | benzene | methylcyclopentane | n-Hexane |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 29.4 | 91.1 | 1.3774 | 0.6648 | 0.9 | 1.3765 | 0.6627 | 0.5 | 1.0 | 4.5 | 94.0 |
| 2 | 28.9 | 93.4 | 1.3774 | 0.6648 | 1.3 | 1.3763 | 0.6623 | 0.7 | 1.3 | 4.0 | 94.0 |
| 3 | 30.3 | 93.1 | 1.3772 | 0.6637 | 1.2 | 1.3761 | 0.6619 | 0.6 | 1.0 | 3.4 | 95.0 |
| 4 | 28.6 | 93.3 | 1.3770 | 0.6635 | 1.0 | 1.3760 | 0.6615 | 0.5 | 1.1 | 3.0 | 95.4 |
| 5 | 27.2 | 96.6 | 1.3768 | 0.6631 | 1.2 | 1.3759 | 0.6613 | 0.6 | 1.0 | 2.9 | 95.5 |
| 6 | 30.1 | 93.3 | 1.3768 | 0.6630 | 1.2 | 1.3758 | 0.6608 | 0.6 | 1.1 | 2.2 | 96.1 |
| 7 | 29.7 | 99.6 | 1.3768 | 0.6630 | 1.3 | 1.3758 | 0.6609 | 0.7 | 1.0 | 2.5 | 95.8 |
| 8 | 28.9 | 93.4 | 1.3767 | 0.6628 | 1.4 | 1.3756 | 0.6608 | 0.8 | 1.1 | 1.9 | 96.2 |
| 9 | 29.4 | 90.0 | 1.3767 | 0.6628 | 1.3 | 1.3756 | 0.6608 | 0.7 | 1.1 | 1.9 | 96.3 |

TABLE 4

Results of the Distillation of the n-Hexane Catalyzate

| Fraction No. | Boiling range, °C (760 mm Hg) | Yield of fraction, % | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|---|
| I | 56.6—67.6 | 1.0 | 1.3760 | 0.6614 |
| II | 67.6—68.9 | 1.5 | 1.3748 | — |
| III | 68.9—69.2 | 86.1 | 1.3749 | — |
| IV | 69.2 | 0.7 | 1.3754 | — |
| Residue | — | 2.6 | — | — |
| Loss | — | 8.1 | — | — |

The fractionation of the combined chromatographed catalyzates (185.3 g), $n_D^{20}$ 1.3760 (3.1% methylcyclopentane), was carried out at a reflux ratio of 240 between plateaus and 100 on a plateau. The results are presented in Table 4. As the constants show, the methylcyclopentane was concentrated in the residue, where the content was 94.7% by refractive index and 96.1% by specific volume. Analysis of the residue by means of Raman spectroscopy showed that it consisted of 95% methylcyclopentane and 5% n-hexane.

## LITERATURE CITED

[1] B. A. Kazanskii and A. L. Liberman et al., Proc. Acad. Sci. USSR, 95, 77 (1954).

[2] B. A. Kazanskii, A. L. Liberman, V. T. Aleksanian and Kh. E. Sterin, Proc. Acad. Sci. USSR, 95, 281 (1954).

[3] A. L. Liberman, T. V. Lapshina and B. A. Kazanskii, Proc. Acad. Sci. USSR, 105, 727 (1955).

[4] A. L. Liberman, T. V. Vasina and B. A. Kazanskii, Proc. Acad. Sci. USSR, 117, 430 (1957).*

[5] B. A. Kazanskii, A. L. Liberman, M. Iu. Lukina and I. V. Gostunskaia, Chem. Sci. and Ind. 2, 172 (1957).

[6] Iu. K. Iur'ev and P. Ia. Pavlov, J. Gen. Chem. 7, 97 (1937).

[7] F. D. Rossini, et al., Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Pittsburgh, 1953.

[8] N. D. Zelinskii and M. V. Turova-Poliak, Coll. Works of N. D. Zelinskii, 2, Izd. AN SSSR, 1941, pp. 150, 224.**

[9] B. A. Kazanskii and T. F. Bulanova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1947, 29.

N. D. Zelinskii Institute of
Organic Chemistry
Academy of Sciences USSR

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*Origianl Russian pagination. See C. B. Translation.

**In Russian.

# THE REACTION OF β-CYANOVINYL KETONES WITH SECONDARY AMINES

Academician A. N. Nesmeianov and M. I. Rybinskaia

In recently published work [1], we have reported on the synthesis of previously unknown derivatives of acrylonitrile – β-cyanovinyl ketones. Preliminary results from a study of the interaction of these compounds with nucleophilic reagents have already demonstrated the high electrophilic activity of their double bonds. Many of these compounds add amines, phenols, and acetoacetic and malonic esters.* It is interesting to note that of the two competitive groups which could direct the orientation of unsymmetrical reagents adding across the double bond, $>C=O$ and $-C\equiv N-$, the carbonyl group is determining, and the orientation is opposite to that which holds for cyanoethylation reactions with acrylonitrile:

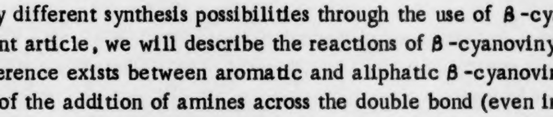
$$CH_2=CHCN + HX \rightarrow XCH_2CH_2CN,$$
$$RCOCH=CHCN + HX \rightarrow RCOCH_2CH(X)-CN.$$

This provides for completely different synthesis possibilities through the use of β-cyanovinyl ketones (β-acylacrylonitriles). In the present article, we will describe the reactions of β-cyanovinylketones with secondary amines. An interesting difference exists between aromatic and aliphatic β-cyanovinyl ketones. Aryl β-cyanovinyl ketones give products of the addition of amines across the double bond (even in the presence of an excess of amine). We prepared products of the addition of diethylamine, piperidine, and morpholine with certain aryl β-cyanovinyl ketones:

$$ArCOCH=CHCN + HNR_2 \rightarrow ArCOCH_2CH(NR_2)-CN,$$

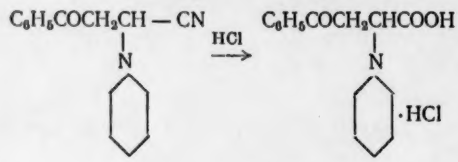
when $Ar = C_6H_5$, $HNR_2 = NH(C_2H_5)_2$, $NHC_5H_{10}$, $NHC_4H_8O$, and
when $Ar = n\text{-}BrC_6H_4$, $n\text{-}NO_2C_6R_4$, $HNR_2 = NHC_4H_8O$.

The resulting addition products are readily crystallizable substances which, however, change on long standing, as was indicated by analyses. Under the influence of alkali, these products of the addition of amines to aryl β-vinyl ketones split out hydrocyanic acid to give aryl β-aminovinyl ketones, which may also be prepared from aryl β-chlorovinyl ketones. Consequently, the addition products are nitriles of α-amino-γ-oxocarboxylic acids. Thus, the action of the calculated amount of alcoholic alkali on α-(N-piperidyl)-β-benzoylpropionitrile yields phenyl β-(N-piperidyl) vinyl ketone, which is identical with that prepared by the alternate synthesis from phenyl β-chlorovinyl ketone and piperidine:



*This material will be published later.

The action of concentrated hydrochloric acid on α-(N-piperidyl)-β-benzoylpropionitrile causes hydrolysis with the formation of the corresponding acid, which we isolated in the form of the stable hydrochloride. α-(N-piperidyl)-β-benzoylpripionic acid, identical to that obtained by the alternate synthesis from β-benzoylacrylic acid and piperidine [2], was obtained by the action of ethylene oxide on this hydrochloride.



On carrying out the hydrolysis of α-(N-morpholinyl)-β-benzoylacrylonitrile under these same conditions, we obtained the amide of the corresponding acid.

It should be noted that the chemistry of the β-aroylacrylic acids, which have been known for a long time, differs slightly. The question of the structure of the products of the addition of ammonia and amines to benzoylacrylic acid has long remained unanswered. Some have considered them α-amino- [2-4] and others β-amino-γ-oxocarboxylic acids [5, 6]. Recently, Cromwell and co-workers showed, indeed by a complex route, that they are α-amino-γ-oxocarboxylic acids [2]. Our route is very simple, and can be used in the future for establishing the structures of other products of additions across the double bond in β-cyanovinyl ketones and β-acylacrylic acids.

Methyl β-cyanovinyl ketone behaves differently under analogous conditions. With diethylamine and piperidine, it exchanges its CN group for an amino group and gives the corresponding methyl β-diethylamino- and methyl β-piperidylvinyl ketones, which are identical with the products of the interaction of methyl β-chlorovinyl ketone with these same amines [7]:

$$CH_3COCH = CHCN + HNR_2 \rightarrow CH_3COCH = CHNR_2,$$

where $HNR_2$ is $(C_2H_5)_2NH$ or $NHC_5H_{10}$.

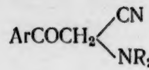
Like methyl β-chlorovinyl ketone, methyl β-cyanovinyl ketone reacts with hydrazine to give 3-methylpyrazole [8]. Thus, in this case the CN group exhibits pseudohalide properties. This should be compared with the appearance of pseudohalide properties of the CN group in the nitrile of pyroracemic acid [9], which is in the nature of a vinylog of methyl β-cyanovinyl ketone. Moreover, the results described naturally lead to the assumption that during the exchange of the CN group, the addition of the amine across the double bond proceeds in the first stage followed by splitting out of hydrocyanic acid. Final judgement on the mechanism of the substitution of the CN group requires a special investigation.

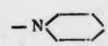
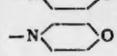
## EXPERIMENTAL

1. Preparation of nitriles of α-amino-β-aroylpropionic acids. To a solution of 0.1 mole of aryl β-cyanovinyl ketone in the minimum amount of benzene was added, while cooling with water, 0.2 mole of amine. Severe cooling was used in the case of diethylamine. The reaction proceeded very rapidly and with the evolution of heat. The precipitated crystals were filtered and washed on the filter with petroleum ether. An additional small amount of the nitrile of the α-amino-β-aroylpropionic acid was obtained from the mother liquor by evaporation. Data on the syntheses are presented in Table 1.

2. Preparation of phenyl β-(N-piperidyl)vinyl ketone from α-(N-piperidyl)-β-benzoylpropionitrile. One g of α-(N-piperidyl)-β-benzoylpropionitrile was agitated for 2 hours with 0.2 g of sodium hydroxide in 10 ml of absolute alcohol. Sodium cyanide precipitated. Absolute ether was added to the reaction mixture to remove the unreacted starting material. The precipitate was filtered. The filtrate was diluted with 70 ml of water and extracted with ether. The solution was dried over sodium sulfate, and the ether evaporated. The yield of phenyl β-(N-piperidyl)vinyl ketone was 0.75 g (85.2% of theoretical); m. p. 86-89° (from alcohol and petroleum ether). A mixture with a known sample, prepared from phenyl β-chlorovinyl ketone by the method of Kochetkov [7], showed no depression of the melting point.

TABLE 1



| Expt. No. | Ar | — $NR_2$ | M. p. in °C | Yield in % | Analytical data | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | | H | | N | | Br | |
| | | | | | found | calc. | found | calc. | found | calc. | found | calc. |
| 1 | $C_6H_5$— | — $N(C_2H_5)_2$ | 79—81 (petroleum ether) | 62 | 72.92 | 73.00 | 8.05 | 7.87 | | | | |
| 2 | $C_6H_5$— |  | 135 alcohol | 95 | 74.29 | 74.38 | 7.63 | 7.43 | 11.45 | 11.57 | | |
| 3 | $C_6H_5$— |  | 130—132 alcohol | 93 | 68.71 | 68.85 | 6.46 | 6.55 | 11.50 | 11.47 | | |
| 4 | *n*-$BrC_6H_4$ |  | 155—156 alcohol | 83.5 | 51.91 | 52.01 | 4.73 | 4.64 | 8.72 | 8.66 | 24.79 | 24.76 |
| 5 | *n*-$NO_2C_6H_4$ |  | 150—153 from acetone | 81.3 | 58.36 | 58.13 | 5.28 | 5.19 | 14.80 | 14.53 | | |

Found %: C 78.28; H 7.82. $C_{14}H_{17}ON$. Calculated %: C 78.13; H 7.90.

3. Hydrolysis of α-(N-piperidyl)-β-benzoylpropionitrile. Three g of the nitrile was dissolved in 25 ml of concentrated hydrochloric acid. Vigorous evolution of heat was observed, and, after 30-40 minutes, a precipitate formed, which again dissolved on standing. A red solution was formed. After standing for a day, the reaction mixture was evaporated to a volume of ~10ml. The precipitated crystals were filtered and washed on the filter with concentrated hydrochloric acid and a small amount of cold alcohol. The yield of α-(N-piperidyl)-β-benzoylpropionic acid hydrochloride was 3 g (81% of theoretical); m. p. 140-143° (from methanol).

Found %: C 60.54; H 6.75; N 4.97. $C_{15}H_{20}O_3NCl$. Calculated %: C 60.50; H 6.77; N 4.70.

α-(N-piperidyl)-β-benzoylpropionic acid was prepared from the hydrochloride by treatment with ethylene oxide; m. p. 166-167.5° with decomposition (from alcohol). A mixture with a sample prepared from β-benzoylacrylic acid and piperidine [2] showed no depression of the melting point.

4. Hydrolysis of α-(N-morpholinyl)-β-benzoylpropionitrile. The hydrolysis was carried out under the same conditions. The yield of α-(N-morpholinyl)-β-benzoylpropionamide hydrochloride was 80% of theoretical; m. p. 148-150° with decomposition (from methanol).

Found %: C 56.23; H 6.54; N 9.63; Cl 11.75. $C_{14}H_{19}O_3N_2Cl$. Calculated %: C 56.29; H 6.36; N 9.38; Cl 11.89.

5. Reaction of methyl β-cyanovinyl ketone with diethylamine. To a solution of 3.4 g of methyl β-cyanovinyl ketone in 20 ml of absolute ether was added 3 g of diethylamine. The reaction was exothermic. After 30 minutes, the ether was distilled, and the residue was distilled under vacuum. The yield of methyl β-diethylaminovinyl ketone was 4 g (74% of theoretical); b. p. 133°/12 mm, $n_D^{20}$ 1.5370. Picrate: m. p. 114-116°. Literature data: b. p. 125/6 mm, $n_D^{20}$ 1.5378; picrate: m. p. 115-116° [7].

6. Reaction of methyl β-cyanovinyl ketone with piperidine. Using an analogous route, methyl β-(N-piperidyl)vinyl ketone was prepared by the interaction of 4 g of methyl β-cyanovinyl ketone and 4 g of piperidine. B. p. 156°/7 mm, $n_D^{20}$ 1.5718. Picrate: m. p. 121-122°. Literature data: b. p. 154-155°/7 mm, $n_D^{20}$ 1.5730; picrate: 122-123° [7].

7. Interaction of methyl β-cyanovinyl ketone with hydrazine. 3-Methylpyrazole was prepared by the reaction of 4 g of methyl β-cyanovinyl ketone with 5 ml of hydrazine hydrate in 10 ml of ether, using the method described for the synthesis of 3-methylpyrazole from methyl β-chlorovinyl ketone [8]. The yield was 0.5 g; b. p. 205-206°/756 mm; $n_D^{21}$ 1.4960. Picrate: m. p. 142-143°. Literature data: b. p. 204-206°/755 mm, $n_D^{14}$ 1.4935. Picrate: m. p. 141-141.5° [8].

## LITERATURE CITED

[1] A. N. Nesmeianov and M. I. Rybinskaia, Proc. Acad. Sci. USSR, 115, No. 2, 315 (1957).*

[2] N. H. Cromwell, P. L. Greger and K. E. Cook, J. Am. Chem. Soc. 78, 4412 (1956).

[3] J. Bougault, Ann. Chim. 15, 498 (1908).

[4] M. M. Fraser and R. A. Raphael, J. Chem. Soc. 1950, 2245.

[5] J. Bougault and P. Chabrier, Compt. rend. 226, 1378 (1948); 230, 212 (1950); 237, 1420 (1953).

[6] R. Delaby, P. Chabrier and S. Danton, Compt. rend. 232, 2326 (1951).

[7] N. K. Kochetkov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, 991.*

[8] A. N. Nesmeianov, N. K. Kochetkov and M. I. Rybinskaia, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1950, 350.

[9] A. K. Kiang, F. G. Mann and A. Topham, J. Am. Chem. Soc. 78, 1319 (1956).

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## KINETICS OF THE HYDROLYSIS OF BORON TRIFLUORIDE COORDINATION COMPOUNDS*

I. G. Ryss

(Presented by Academician A. V. Topchiev, February 5, 1958)

We have found that the kinetics of the hydrolysis of compounds of the type $F_3B:Am$, where Am is an amine, depends not only quantitatively, but also qualitatively on the nature of the amine.

The first analytically determinable stage of the hydrolysis of these compounds is apparently irreversible, and is described by the equation

$$F_3B:Am + H_2O = AmH^+ + BF_3OH^-. \qquad (1)$$

In neutral or acid medium, reaction (1) is complicated by the partial conversion of $BF_3OH^-$ to $BF_4^-$ [1]; in alkaline medium, $BF_3OH^-$ undergoes rapid quantitative decomposition to borate and fluoride.

The decomposition of the boron trifluoride-pyridine complex $F_3B:NC_5H_5$ in alkaline medium is a relatively fast first-order reaction; hydrolysis in neutral or acid medium proceeds with the same rate [2]. Hydrolysis of $F_3B:NC_5H_5$ is not accelerated by $F^-$ ions, which accumulate in an alkaline medium to the extent to which the complex decomposes.

A previous attempt [3] to study the kinetics of the hydrolysis of $F_3B:NH_3$ did not yield quantitative data owing to the complexity caused by the conversion of $BF_3OH^-$ to $BF_4^-$. In the present work, a new method was used to study the kinetics of the hydrolysis of $F_3B:NH_3$; this method is based on the determination of the concentration of $F_3B:NH_3$ remaining unhydrolyzed at a given time. The determination was based on the slowness of the hydrolysis of $F_3B:NH_3$ in neutral or acid solution and its rapid decomposition in a strongly alkaline medium; a cooled sample of the solution being investigated was neutralized to a methyl orange end-point in the presence of an excess of $CaCl_2$, an excess of standard base was then added to the sample until an intense thymolphthalein color was obtained, and then, after 10-15 minutes, the excess base was back-titrated with acid to a methyl orange end-point. With this procedure, the consumption of base corresponds to the equation

$$2F_3B:NH_3 + 3Ca^{2+} + 4OH^- + 2H_2O = 2NH_4^+ + 2H_3BO_3 + 3CaF_2\downarrow. \qquad (2)$$

This same method was also used for the study of the kinetics of the hydrolysis of $F_3B:NH_2CH_3$.

The rates of hydrolysis of $F_3B:NH_3$ and $F_3B:NH_2CH_3$ were low; hydrolysis proceeded according to a first-order equation, and it was neither catalyzed nor inhibited by $H^+$ ions (in experiments in $\sim$0.25 N HCl). Hydrolysis of both compounds was accelerated by the presence of $F^-$ ions; it was simultaneously retarded by the formation of $BF_4^-$. The rate of hydrolysis in the presence of $F^-$ ions was approximately proportional to their concentration; with a constant concentration of NaF during the course of the experiment, the hydrolysis was a first-order reaction; however, the rate constant determined under these conditions is the sum of two values:

$$k_F = k + k_2[F], \qquad (3)$$

where $\underline{k}$ is the rate constant for the hydrolysis in water, and $k_2^-$ is the rate constant for a second-order process (in moles$^{-1}$ · liters · minutes$^{-1}$). Acidification of the NaF solution to a pH of 5.2 did not eliminate the catalytic action of $F^-$.

The temperature dependence of the rate constant $\underline{k}$ was quite well expressed by the usual relation

$$\lg k' \equiv \lg (0.4343k) = A - \frac{B}{T}. \tag{4}$$

The quantitative characteristics of the kinetics of the hydrolysis of the substances investigated are presented in Table 1, in which data are also included for the hydrolysis of $BF_4^-$ (the reaction is first-order, and is catalyzed by $H^+$ ions) [4]; values calculated for the hydrolysis rate constant at 25° are also included.

TABLE 1

| Compound investigated | Temperature region, °C | Coefficients for Equation (4) A | Coefficients for Equation (4) B | 0.4343 $\underline{k}$ at 25°, min.$^{-1}$ | E, kcal. | $\Delta S^{\neq}$ e.u. |
|---|---|---|---|---|---|---|
| $BF_4^-$ (dil. soln.) | 20—80 | 7.11 | 3730 | $3.98 \cdot 10^{-6}$ | 17.1 | —34 |
| $BF_4^-$ (conc. soln.) | 20—80 | 7.554 | 3921.5 | $2.52 \cdot 10^{-6}$ | 17.95 | —32 |
| $F_3B : NC_5H_5$ | 0—30 | 12.82 | 4448 | $7.94 \cdot 10^{-3}$ | 20.3 | — 8.3 |
| $F_3B : NH_3$ | 25—80 | 14.70 | 5945 | $5.75 \cdot 10^{-6}$ | 27.2 | 0.3 |
| $F_3B : NH_2CH_3$ | 70—100 | 15.95 | 6845 | $9.8 \cdot 10^{-8}$ | 31.3 | 6.0 |

The apparent activation energy for $F_3B : NH_3$, calculated for a second-order process from the temperature dependence of $k_2$, agreed substantially with that found for the hydrolysis; in the temperature range studied (25-80°), log $k_2$ was 0.9 larger than log $\underline{k}$. For $F_3B : NH_2CH_3$, the temperature dependence of log $k_2$ is given by the equation

$$\lg k_2 = 13.64 - \frac{5600}{T}; \quad E_2 = 25.6 \text{ kcal.} \tag{5}$$

The hydrolysis of $F_3B : NH_2CH_3$ was sharply accelerated in $NaHCO_3$ solutions saturated with carbon dioxide; it was especially sharply accelerated if the carbon dioxide was removed from the solution, thereby increasing the concentration ratio $[CO_3^{2-}] / [HCO_3^-]^2$; consequently, $CO_3^{2-}$ ions catalyze the hydrolysis more strongly than $HCO_3^-$ ions.

According to our preliminary data, the hydrolysis of $F_3B : NH(CH_3)_2$ is catalyzed by $F^-$ and $OH^-$ ions, and it proceeds at almost the same rate as the hydrolysis of $F_3B : NH_2CH_3$. The rate of hydrolysis of $F_3B : NH_2C_6H_5$ could not be studied quantitatively, since the material is only sparingly soluble in water; in NaOH solutions, this substance decomposes very rapidly, the decomposition rate apparently being limited by the rate at which it dissolves.

Discussion. Since the rates of hydrolysis of $F_3B : NC_5H_5$ and $BF_4^-$ do not depend on the basicity of the solution, they must be determined by the rates of solvolytic dissociation of the complexes; the high electronegativity of fluorine and the structure of the electron cloud of boron provide a basis for the assumption that these processes are $S_N1$ nucleophilic substitutions. This is also true of the hydrolysis of complexes of $BF_3$ with $NH_3$ and $NH_2CH_3$; they decompose rapidly in a strongly basic medium, but the rate of hydrolysis is not determined by $OH^-$ ions arising through the dissociation of water – this is shown by the fact that the hydrolysis of the complexes is not retarded by the presence of HCl.

Acceleration of the hydrolysis of complexes of $BF_3$ with $NH_3$ and $NH_2CH_3$ in the presence of $F^-$ ions is not the result of the reaction taking place by the mechanism usually assumed for $S_N2$ processes (an attack on the complexes by $F^-$ ion, replacing the amino group), since in such cases decomposition of the complexes

would be accompanied by the formation of equivalent amounts of $BF_4^-$, which is contradictory to experiment; moreover, the substitution of the amino group by $F^-$ or by the more nucleophilic $OH^-$ should proceed more readily in the less stable complex of $BF_3$ with pyridine.

The catalytic action of $F^-$ is perhaps explained by the following hypothesis: coordination of ammonia to boron trifluoride, which is accompanied by donation of an electron pair by N to B, increases the acid properties of the hydrogen of the ammonia and its ability to form hydrogen bonds (this is apparent in, for example, the ability of $F_3B:NH_3$ to add a molecule of ammonia [5]). In connection with this, a rapidly established equilibrium exists in the solution:

$$F_3B:NH_3 + F^- \rightleftarrows F_3B:NH_3...F^- \quad (6)$$

The addition of a negative ion must weaken the [B ← N] bond in the complex and facilitate its solvolytic dissociation; if this process also proceeds by an $S_N1$ mechanism, the overall rate of hydrolysis of $F_3B:NH_3$ will be given by the equation

$$-\frac{dC}{dt} = kC + k_2C\,[F^-] = k_FC, \quad (7)$$

where C is the concentration of $F_3B:NH_3$. Equation (3) follows from Equation (7). The constant $k_2$ is the product of the rate constant for the hydrolysis of $BF_3:NH_3...F^-$ and the equilibrium constant for the formation of this complex; the apparent activation energy is, consequently, the sum of the activation energy and the heat of formation of $E_2$ from $F_3B:NH_3$ and $F_3B:NH_3...F^-$ and $F_3B:NH_3$ and $F^-$.

The acceleration of the decomposition of $F_3B:NH_3$ and $F_3B:NH_2CH_3$ in the presence of $HCO_3^-$, $CO_3^{2-}$, and $OH^-$ ions is apparently caused by similar processes; direct rupture of the [B ← N] bond as the result of an attack on the complexes by these ions seems improbable if one compares, as above, their properties and those of $F_3B:NC_5H_5$.

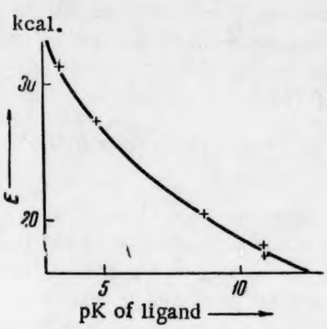



Fig. 1. Dependence of the energy of activation of the hydrolysis of $BF_3$ complexes on pK of the basic dissociation of the ligands. Ligands: 1) $F^-$, 2) $NC_5H_5$, 3) $NH_3$, 4) $NH_2CH_3$.

With the mechanism assumed for the hydrolysis of the complexes, the action of the various anions must increase, as in the case of an $S_N2$ mechanism, in the order of increasing basic properties ($F^- < HCO_3^- < CO_3^{2-} < OH^-$); these anions must also accelerate the hydrolysis of compounds of $BF_3$ with other primary and secondary amines, but not with tertiary amines. This is in agreement with the distinct qualitative difference between the kinetics of the hydrolysis of $BF_4^-$ or $F_3B:NC_5H_5$ and those of the hydrolysis of compounds of $BF_3$ with $NH_3$, $NH_2CH_3$, $NH(CH_3)_2$, and $NH_2C_6H_5$.

Another possible explanation leads to the same conclusions; the increase in the pH of a solution containing the ions $F^-$, $HCO_3^-$ etc. promotes the dissociation of $F_3B:NH_3$ into $H^+$ and $F_3B:NH_2^-$ which hydrolyzes more rapidly than the neutral complex; during the study of the hydrolysis rates in water, the rapid decrease in pH suppressed the dissociation of the $F_3B:NH_3$ and eliminated its effect on the rate of hydrolysis.

Figure 1 shows that the activation energy of the hydrolysis of boron trifluoride complexes increases regularly with an increase in the basic properties of the ligands; a connection exists between the thermodynamic properties of the ligand and the transition state. In spite of the relatively low value of E, the hydrolysis of $BF_4^-$ is slow owing to the very low entropy of activation, $\Delta S^{\neq}$. It is well known [6] that in a number of cases the change in $\Delta S^{\neq}$ for a series of analogous reactions is proportional to the standard entropy changes of the processes,

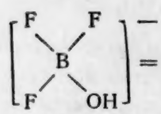
$\Delta S^0$. It can be shown that the difference in $\Delta S^0$ for the dissociation of $BF_4^-$ and $F_3B:NH_3$ in the gas phase is large, since $F^-$ does not have a rotational contribution to its entropy. However, the effect of the change in symmetry number and of the change in the number of vibrational degrees of freedom decrease this difference; approximate calculations based on the use of the equations of statistical thermodynamics have shown that this difference does not exceed a few entropy units.

Consequently, if a proportionality exists between $\Delta S^{\neq}$ and $\Delta S^0$, the second value depends essentially on the effect of solvation; the effect of solvation on $\Delta S^{\neq}$ is confirmed by the fact that the hydrolysis of $BF_4^-$ in an aqueous-alcoholic medium [7] proceeds more slowly than in water, owing to a decrease in $\Delta S^{\neq}$. Ordering of the structure of water through the action of the ion field leads to a decrease in the entropy; the effect of the small $F^-$ is greater than that of the larger $BF_4^-$. The effect of solvation on $\Delta S^0$ of the dissociation of $BF_3$ complexes with amines must be smaller.

A proportionality between entropy and entropy of activation is sometimes apparent for a series of analogous reactions [8]. Indeed, for $F_3B:Am$ the relationship $\Delta S^{\neq} = 1.325\,E - 35.4$ exists (see Table 1), but this equation does not apply to the kinetics of the hydrolysis of $BF_4^-$.

$H^+$ ions catalyze the hydrolysis of $BF_4^-$, $SO_3F^-$, $PF_6^-$, and,probably, other complex fluorine-containing anions owing to outer sphere association caused by the attraction of the ionic charges; this facilitates the elimination of HF. This mechanism is excluded for neutral molecules $F_3B:Am$; the addition of $H^+$ to an unshared pair of electrons on one of the fluorine atoms of the complex does not proceed to such an extent that it affects the kinetics of the hydrolysis.

The rapid decomposition of $BF_3OH^-$ in a basic medium is apparently connected with an inner sphere transfer of a proton and the subsequent processes of HF elimination and the addition of water:


$= HF + F_2BO^-$

$$F_2BO^- + H_2O = [F_2B(OH)_2]^- = HF + FB(OH)O^- \qquad \text{etc.}$$

An analogous explanation holds for the rapid decomposition by a base of other fluorine-containing complexes of boron, for example, $K_2[B_3O_3F_4OH]$ or $Na_3[B_3O_3F_6]$ [1] (in this case, a dynamic equilibrium exists between $B_3O_3F_6^{3-}$ and $BOF_2^-$ or $F_2B(OH)_2^-$). This same mechanism also explains the rapid decomposition of hydroxyfluorine complexes of a number of other elements, for example $[AsF_5OH]^-$ [9].

The high rate of hydrolysis of compounds of $BF_3$ with ethers, alcohols, etc. is connected with the weakness of the basic properties of the ligands.

The kinetics of the hydrolysis of fluorine-containing complexes of the majority of other elements has not been studied, and hypothesizing on the mechanism of their hydrolysis can have no quantitative basis. It is possible that the slow hydrolysis of coordinately saturated $PF_6^-$ and $AsF_6^-$ proceeds by an $S_N1$ mechanism in which, as in the case of $BF_4^-$, $\Delta S^{\neq}$ has a high negative value; the values of E for these compounds, which are thermodynamically unstable in aqueous solutions, are hardly high. The rapid hydrolysis of the hexafluoro complexes of the transition metals ($VF_6^-$, $NbF_6^-$) can be connected with the addition of molecules of water (due to the unfilled d-bands of the metal atoms) and to the elimination of HF as a result of inner-sphere transfer of protons.

## LITERATURE CITED


[1] I. G. Ryss, The Chemistry of Fluorine and Its Inorganic Compounds, Moscow, 1956.*

[2] I. G. Ryss and S. L. Idel's, J. Inorg. Chem. 2, 2716 (1957).

[3] I. G. Ryss and N. P. Pisarzhevskaia, Proc. Acad. Sci. USSR, 87, 995 (1952).

[4] I. G. Ryss and M. M. Slutskaia, J. Phys. Chem. 21, 549 (1947).


* In Russian.

[5] H. C. Brown and S. Johnson, J. Am. Chem. Soc. 76, 1978 (1954).

[6] S. Glasstone, K. Laidler and H. Eyring, The Theory of Absolute Reaction Rates [The Theory of Rate Processes. The Kinetics of Chemical Reactions, Viscosity, Diffusion, and Electrochemical Phenomena], Foreign Lit. Press, 1948, p. 147 (Translation).

[7] I. G. Ryss and V. A. Plit, J. Gen. Chem. 25, 19 (1955).*

[8] E. A. Moelwyn-Hughes, The Kinetics of Reactions in Solutions, Moscow-Leningrad, 1938, pp. 135-136. (Translation).

[9] H. M. Dess and R. W. Parry, J. Am. Chem. Soc. 79, 1589 (1957).

Dnepropetrovsk Institute of
Railway Transport Engineers

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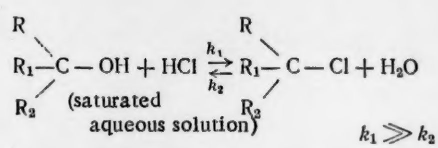
# HYDROGEN-EXCHANGE REACTIONS OF ALKYL CHLORIDES WITH HYDROCHLORIC ACID AND OF TERTIARY BUTYL ALCOHOL DURING THE SUBSTITUTION OF HYDROXYL BY CHLORINE

V. N. Setkina and Corresponding Member AN SSSR D. N. Kursanov

The reaction of tertiary aliphatic alcohols with a saturated aqueous solution of hydrogen chloride proceeds at a high rate and practically irreversibly with the formation of the corresponding alkyl chlorides.




There are no reliable data in the literature on the mechanism of this reaction; however, the mechanism of the reverse reaction – the hydrolysis of tertiary alkyl chlorides – has been established [1], and is a monomolecular nucleophilic substitution reaction ($S_N1$).

It may be assumed that the reaction forming tertiary chlorides from the corresponding alcohols proceeds by a carbonium ion mechanism.

In the present work, our investigation was directed toward a determination of whether this reaction is accompanied by hydrogen exchange. It is evident that the presence of deuterium in the resulting chlorides would serve as an indication of the formation in an intermediate stage of this reaction of a rather long-lived carbonium ion [2].

With this aim, the reaction of tertiary butyl alcohol with a saturated aqueous solution of hydrochloric acid enriched with deuterium was investigated. The investigation showed that the tertiary butyl chloride, which formed at a high rate, contained only an insignificant amount of deuterium. Moreover, on further contact of the chloride with hydrochloric acid-d, the deuterium content of the tertiary butyl chloride increased; for example, with a 38-hour contact time, the depth of exchange exceeded 30%* (Table 1). Similar results were obtained with other tertiary chlorides: tertiary amyl chloride and 1-methyl-1-cyclohexyl chloride.

It was established that the number of hydrogen atoms exchanging with deuterium corresponded only to the number of $\alpha$-hydrogen atoms. Under these same conditions, a primary chloride – butyl chloride – did not enter into the hydrogen-exchange reaction (Table 2).

Numerous investigations [4] of the mechanism of various solvolytic reactions of tertiary alkyl halides have shown that all of these reactions take place by an $S_N1$ mechanism, and the stage determining their rate

*Our data regarding the absence of hydrogen exchange during the course of the reaction of tertiary alcohols with hydrochloric acid are in agreement with the data of Shull and co-workers [3], who established that during the course of the preparation of tertiary butyl-$d_9$ chloride from tertiary butyl-$d_9$ alcohol and hydrochloric acid, there is no observable hydrogen-deuterium exchange. However, on the basis of the present investigation it must be considered that there is a significant change in the isotope composition of the chlorides during lengthy contacting of the components.

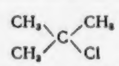
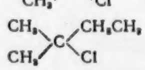
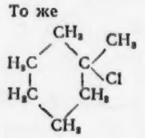
is the ionization of the tertiary halides. It is evident that this reaction of tertiaryhalides with hydrochloric acid-d must also be a particular case of solvolytic monomolecular reactions. On this basis, it would seem that the hydrogen exchange reaction of tertiary alkyl halides is connected with their ability to ionize in a hydrochloric acid solution, which has a high dielectric constant. The nature of the ionization of the chlorides can vary from a state of ion pairs to solvated carbonium ions. Hydrogen exchange is a consequence of the ionization of the chlorides.

TABLE 1

| Expt. No. | Alcohol | Experimental conditions: mole ratio alcohol/DCl | Experimental conditions: reaction time | EDCW* of chloride, γ/ml: calc. for exchange of all H | EDCW* of chloride, γ/ml: found | Exchange, % of calc. |
|---|---|---|---|---|---|---|
| 1 | $(CH_3)_3C-OH$ | 1 : 1 | 10 min. | 7800 | 30 | 0.4 |
| 2 | Same | 1 : 1.34 | 20 " | 42960 | 1000 | 2.3 |
| 3 | " " | 1 : 1.42 | 10 " | 40750 | 445 | 1.1 |
| 4 | " " | 1 : 1.42 | 38 hours | 40750 | 12470 | 31.0 |

*Here and elsewhere, EDCW denotes excess density of combustion water.

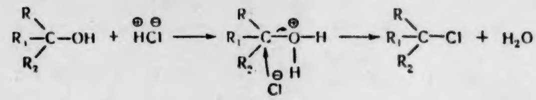
TABLE 2

| Expt. No. | Chloride | Expt. conditions: mole ratio chloride/DCl | Expt. conditions: reaction time, hours | EDCW of chloride, γ/ml: calculated for all H | EDCW of chloride, γ/ml: calculated for α-H | EDCW of chloride, γ/ml: found | Exchange, % of calculated for α-H |
|---|---|---|---|---|---|---|---|
| 1 |  | 1 : 3.6 | 105 | 58200 | 58200 | 55700 | 96.0 |
| 2 |  | 1 : 2.4 | 113 | 47030 | 38570 | 30530 | 79.2 |
| 3 | То же | 1 : 3.3 | 250 | 37820 | 30250 | 29890 | 98.8 |
| 4 |  | 1 : 3.4 | 106 | 50800 | 32970 | 23240 | 70.5 |
| 5 | Same | 1 : 2.9 | 250 | 38810 | 20480 | 18590 | 90.7 |
| 6 | $n-C_4H_9Cl$ | 1 : 4.5 | 110 | 31900 | 31900 | 414 | 1.3 |

The fact that only the α-hydrogen atoms of the chlorides participate in the hydrogen exchange could be due to the impossibility, under the conditions investigated, of the carbonium ion center migrating along the carbon atom chain owing to the attraction of the carbonium ion center for the anions (in ion pairs); or it could be due to the effect exerted by the solvate shell of the carbonium carbon (in free carbonium ions).

The absence of deuterium in the tertiary butyl chloride formed as a result of the fast process of nucleophilic substitution of hydroxyl by chlorine during the interaction of tertiary butyl alcohol with hydrochloric acid-d, permits the assumption that either carbonium ions are not formed at all during the course of this reaction or their lives are so short that they cannot exchange to any appreciable extent with the acid donors of deuterium.

Apparently, the first proposal is the more probable. An instance, described in the literature [5], in which optical activity is retained during substitution of hydroxyl by chlorine at an asymmetric carbon supports this viewpoint. This concept corresponds to a synchronous reaction mechanism:



## EXPERIMENTAL METHODS*

Reaction of tertiary butyl alcohol with a saturated aqueous solution of HCl. I. 7.55 g (102 mmoles) of tertiary butyl alcohol, freshly distilled over calcium hydride, was agitated for 10 minutes with 11.55 g (125 mmoles HCl) of 40% hydrochloric acid having an excess density of 10,000 $\gamma$/ml. The chloride layer was washed with ice water, bicarbonate solution, again with water, dried over $CaCl_2$, and distilled. The resulting chloride had the following constants: b. p. 52°, $n_D^{20}$ 1.3847, $d_4^{20}$ 0.8425, EDCW 30 $\gamma$/ml. The EDCW calculated for the exchange of 9 H is 7800 $\gamma$/ml. The investigation showed that hydrogen exchange does not occur during the exchange of the hydroxyl of an alcohol for chlorine under the influence of HCl.

II. 7.61 g (103 mmoles) of tertiary butyl alcohol and 12.71 g (138 mmoles HCl) of a saturated solution of hydrochloric acid having an excess density of 79,000 $\gamma$/ml were agitated for 20 minutes. The resulting tertiary butyl chloride had the following constants: b. p. 50-51°, $n_D^{20}$ 1.3848, $d_4^{20}$ 0.8400, EDCW 1000 $\gamma$/ml. The EDCW calculated for the exchange of 9 H is 42,960 $\gamma$/ml.

III. 7.80 g (105 mmoles) of tertiary butyl alcohol was agitated with 12.6 g (138 mmoles HCl) of hydrochloric acid having an excess density of 80,500 $\gamma$/ml. A sample of the chloride taken after 10 minutes had the following constants: b. p. 50-50.5°, $n_D^{20}$ 1.3850, $d_4^{20}$ 0.8436, EDCW 445 $\gamma$/ml. The chloride separated after 38 hours of agitation had a b. p. of 49-50°, $n_D^{20}$ 1.3841, $d_4^{20}$ 0.8519, EDCW 12,470 $\gamma$/ml. The EDCW calculated for isotope equilibrium is 40,750 $\gamma$/ml.

Hydrogen exchange between tertiary butyl chloride and hydrochloric acid. 3.95 g (43 mmoles) of tertiary butyl chloride (b. p. 52°, $n_D^{20}$ 1.3852, $d_4^{20}$ 0.8435) and 14.17 g (155 mmoles HCl) of a saturated aqueous solution of hydrochloric acid having an excess density of 80,500 $\gamma$/ml were agitated in a sealed tube for 105 hours. The resulting chloride had a b. p. of 51-52°, $n_D^{20}$ 1.3830, $d_4^{20}$ 0.8899, EDCW 55,700 $\gamma$/ml. The EDCW calculated for the exchange of 9 H is 58,200 $\gamma$/ml.

Hydrogen exchange between tertiary amyl chloride and hydrochloric acid. I. 4.1 g (38.5 mmoles) of tertiary amyl chloride (b. p. 82°, $n_D^{20}$ 1.4043, $d_4^{20}$ 0.8627) and 8.38 g (91.8 mmoles HCl) of hydrochloric acid having an excess density of 80,500 $\gamma$/ml were agitated for 113 hours. The resulting chloride had a b. p. of 83°, $n_D^{20.3}$ 1.4016, $d_4^{20}$ 0.8954, EDCW 30,530 $\gamma$/ml. The EDCW calculated for the exchange of 8 H is 38,570 $\gamma$/ml.

II. 2.48 g (23.3 mmoles) of the chloride and 6.94 g (76 mmoles HCl) of hydrochloric acid (80,500 $\gamma$/ml) were agitated for 250 hours. The EDCW of the chloride after the experiment was 29,890 $\gamma$/ml; the EDCW calculated for the exchange of 8 $\alpha$-H is 30,250 $\gamma$/ml.

Hydrogen exchange between 1-methylcyclohexyl chloride and hydrochloric acid. I. 3.28 g (25 mmoles) of 1-methylcyclohexyl chloride (b. p. 58°/30 mm, $n_D^{20}$ 1.4572, $d_4^{20}$ 0.9666) and 7.70 g (84 mmoles HCl) of hydrochloric acid (80,500 $\gamma$/ml) were agitated for 106 hours. The resulting chloride had a b. p. of 69-70°/42-43 mm, $n_D^{20}$ 1.4567, $d_4^{20}$ 0.9967, EDCW 23,240 $\gamma$/ml. The EDCW calculated for the exchange of 7 $\alpha$-H is 32,970 $\gamma$/ml.

II. 3.33 g (25 mmoles) of methylcyclohexyl chloride and 6.37 g (73 mmoles HCl) of hydrochloric acid (42,000 $\gamma$/ml) were agitated for 250 hours. The resulting chloride had a b. p. of 49.5°/24-25 mm, $n_D^{20}$ 1.4569, $d_4^{20}$ 0.9920, EDCW 18,590 $\gamma$/ml. The EDCW calculated for the exchange of 7 $\alpha$-H is 20,480 $\gamma$/ml.

Hydrogen exchange between normal butyl chloride and hydrochloric acid. 2.25 g (24 mmoles) of n-butyl chloride (b. p. 78°, $n_D^{20}$ 1.4015, $d_4^{20}$ 0.8850) and 9.91 g (109 mmoles HCl) of hydrochloric acid (41,870 $\gamma$/ml)

* A. N. Astakhova and L. E. Andreeva assisted in the experimental work.

were agitated for 110 hours. The resulting chloride had a b. p. of 77-78°, $n_D^{20}$ 1.4014, $d_4^{20}$ 0.8869, EDCW 414 γ/ml. The EDCW calculated for the exchange of 9 H is 31,900 γ/ml.

## LITERATURE CITED


[1] L. C. Batemen and E. D. Hughes, J. Chem. Soc. 1940, 935; E. D. Hughes, J. Chem. Soc. 1935, 225; K. A. Cooper and E. D. Hughes, J. Chem. Soc., 1937, 1183; C. K. Ingold, Structure and Mechanism in Organic Chemistry, London, 1953, p. 308.

[2] J. W. Otvos, L. P. Stewenson, C. D. Wagner and O. Beeck, J. Am. Chem. Soc. 73, 5741 (1951); 74, 3269 (1952); D. N. Kursanov and V. V. Voevodskii, Prog. Chem. 23, 641 (1954); V. N. Setkina, D. N. Kursanov and E. V. Bykova, Problems of Kinetics and Catalysis, 9, 234, 1957.*

[3] E. R. Shull, T. S. Oakwood and D. H. Rank, J. Chem. Phys. 21, 2024 (1953).

[4] L. C. Bateman and M. G. Church, et al., J. Chem. Soc. 1940, 979; L. C. Bateman and E. D. Hughes, J. Chem. Soc. 1937, 1187; 1940, 954; W. Koskoski, H. Thomas and R. D. Fowler, J. Am. Chem. Soc. 63, 2451 (1941).

[5] W. Hückel and H. Pietrzok, Lieb. Ann. 540, 250 (1939); W. A. Cowdrey and E. D. Hughes, et al., J. Chem. Soc. 1937, 1267; E. D. Hughes, C. K. Ingold and J. C. Whitfield, Nature, 147, 206 (1941); E. R. Alexander, Principles of Ionic Organic Reactions, N.Y., 1950, p. 92.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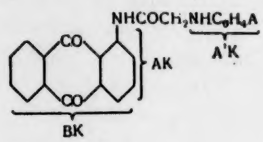
# COLOR EFFECTS IN N-PHENYLGLYCYL DERIVATIVES OF α-AMINOANTHRAQUINONE

E. A. Smirnov

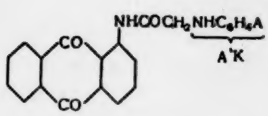
(Presented by Academician B. A. Kazanskii, January 22, 1958)

The derivatives of α-aminoanthraquinone considered in the present communication can be classed with those compounds having two electron donor systems, i.e., with compounds which have besides an electrophilic chromorphoric system, two electron donor systems which are not conjugated with each other. These compounds correspond to the general formula I, where A is H, $CH_3$, $OCH_3$ in an o-, m-, or p-position with respect to the NH.

I 


Derivatives of anthraquinone with one substituent in the α- or β-position have been studied in detail by numerous investigators [1-8]; however, compounds of the type of I have not been described in the literature.

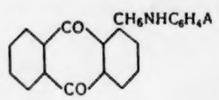
TABLE 1

Color of Compounds of the Type 


| A'K electron donor system | | Color of the substance | |
|---|---|---|---|
| | | in crystals | in powder |
| $-NHC_6H_5$ | (II) | Light red | Orange-red |
| $-NHC_6H_4CH_3$-o | (III) | Orange | Yellow-orange |
| $-NHC_6H_4CH_3$-m | (IV) | Red | Brownish red |
| $-NHC_6H_4CH_3$-p | (V) | Cherry red | Brown-red |
| $-NHC_6H_4OCH_3$-o | (VI) | Red | Brick red |
| $-NHC_6H_4OCH_3$-m | (VII) | " | |
| $-NHC_6H_4OCH_3$-p | (VIII) | Claret red | Red-brown |
| $-NHC_{10}H_7$-α | (IX) | Violet-red | Claret red |
| $-NHC_{10}H_7$-β | (X) | Dark red | Cherry red |

In contrast to compounds, previously studied by us, which contained two electron donor systems and in which the electrophilic system was an acylnitrobenzoic acid (m- or p-) [9] or an acyl-3,5-dinitrobenzoic acid [10], the electrophilic system BK in compounds of the present type is an anthraquinone molecule. The latter is a stronger chromophoric system than acylnitrobenzoic acids; this is apparent if only from the fact that anthraquinone has a visible color (yellow), while nitrobenzoic acid is colorless. The acylamino group together with the double bonds of one of the anthraquinone rings to which it is attached may be considered as the first electron donor system (AK). It is true that this ring simultaneously enters into the make-up of the electrophilic system, since actually the CO and NHAc groups in the present case are parts of the same chromophoric system. Conditionally, however, such compounds must be considered as "compounds with superimposed chromophoric systems" [11]. The second electron donor system (A'K) is separated from the electrophilic system by a series of groups which disrupts the conjugation of the double bonds, and thus is an "isolated chromophoric system." The systems AK and A'K differ greatly with respect to their electron donor properties. The system AK exhibits only very weak electron donor properties, since the ability to donate of the amino group entering into the composition of this system is suppressed to a considerable extent by the acyl group attached to it. Therefore, α-chloroacetamidoanthraquinone (I) – which was the starting material for the compounds under consideration, and which has only one electron donor system, AK – is only colored yellow.

The system A'K is a considerably stronger electron donor system, since it contains an amino group unweakened with respect to donating ability by acylation, and, moreover, this system is strengthened by the presence of a second electron donor group, $CH_3$ or $OCH_3$. As may be seen from Table 1, all compounds containing the system A'K have considerably deeper color than the mother compound (I), which contains only the system AK. Hence, we may make the following basic conclusion: the comparatively deeper colors of the compounds under consideration are due to the interaction of the systems A'K and BK. But since these systems are not conjugated with each other, this interaction must be accomplished through exomolecular forces [12]; The presence in the anthraquinone nucleus of a NHAc group is, in the present case, an unfavorable factor for the appearance of color, since it decreases the electrophilic properties of the system BK to some extent and thereby leads to a lighter-colored compound. Therefore, it would be expected that, for example, compounds having structures in accordance with Type II (analogous to our previously considered nitrobenzyl derivatives [13]), in which the same electron donor system, A'K, but not an acylamido group, is present, will have a deeper color than the present compounds.

II 


Further, it is interesting to note that not one of the compounds under consideration can be obtained in a less deeply colored form, the color of which can be explained by the interaction of the systems BK and AK with disruption of the interaction between the systems BK and A'K. Such forms have been isolated by us [9, 10] in other series of compounds with two electron-donor groups. The explanation of this must apparently be sought in the fact that the electrophilic system in anthraquinone derivatives is considerably stronger, and, therefore, its interaction with the system A'K, which occurs in the substance in the solid state, is more difficultly disrupted.

As regards the absorption spectra of anthraquinone derivatives containing various substituents in the α- and β-positions, they have been studied in detail by a number of investigators [4-8], and, therefore, we shall limit ourselves to the presentation of only three absorption curves. A feature of the present compounds is the presence in their substituent (the acylamido group) of a second electron donor system (isolated). In Fig. 1 are presented the absorption curves for two compounds containing both electron donor systems (AK and A'K) and for one compound which has only the system AK. In considering these curves, we first of all direct attention to the high degree of similarity among them in spite of the fact that the compounds corresponding to them differ considerably in color when in the solid state. Thus, for example, the compound which does not contain the system A'K (I) is yellow, and the compound with a p-$CH_3$ group (V) is cherry-red. In this respect, the absorption curves are substantially different from those for reflected light, which indicate a difference in the color of these three compounds (Fig. 1). This similarity among these absorption curves, which is apparent both with respect to

form and with respect to the position of the maxima, can be considered evidence that the basic factor dictating the comparatively deep color in the solid state of the compounds being considered, namely, the interaction of the electron donor system A'K with the electrophilic system BK by means of exomolecular forces [12], is absent in highly dilute solutions. However, in more concentrated solutions ($0.5 \cdot 10^{-2}$ M, in pyridine), this interaction begins to appear, and in the corresponding curves (Fig. 2) two absorption bands appear in the visible region. As seen from these curves, this band is still quite undetectable in solutions which are ten times less concentrated.

In conclusion, it should be noted that all of the compounds synthesized by us possess the properties of vat dyes: they are reducible by sodium hydrosulfite [sodium dithionite] giving an intense red color to the vat in which cotton fiber is dyed, though only to a light cream color (various shades). This indicates the low substantivity of the present dyes.

## EXPERIMENTAL

The starting material for the preparation of the compounds under consideration was α-chloroacetamidoanthraquinone (I), which we synthesized by the method of reference [14]. M. p. 220.5-220.8° (not described in the literature).

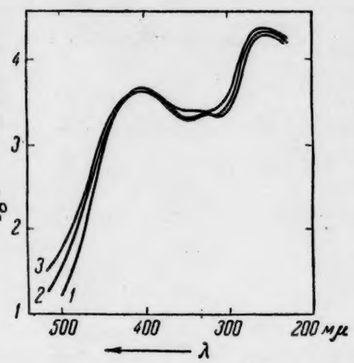



Fig. 1. Absorption curves of α-aminoanthraquinone derivatives of the type:

$$C_6H_4 \left\langle {CO \atop CO} \right\rangle C_6H_3NHCOCH_2\overbrace{NHC_6H_4A}^{A'K}$$

1) α-chloroacetamidoanthraquinone, 2) A'K = $= NHC_6H_5$, 3) A'K = $NHC_6H_4CH_3$ (para) (in dichloroethane).

N-(p-Tolylglycyl)-1-aminoanthraquinone (V). A mixture of (I) and p-toluidine (1 : 2 mole ratio) was heated for an hour on an oil bath at a temperature of 110-115°. The cooled mixture was treated with dilute HCl, and was then washed with water, a solution of soda, and again with water. After recrystallization from chlorobenzene, the product was obtained in the form of cherry-red prisms with a m. p. of 250.5-251.0°.

Found %: N 7.53. $C_{23}H_{18}O_3N_2$. Calculated %: N 7.57.

All succeeding preparations were prepared in an analogous manner. The only changes were occassional variations in the temperature and the time of heating; these will be indicated in the individual cases.

N-(m-Tolylglycyl)-1-aminoanthraquinone (IV). The product was recrystallized from toluene. The red prismatic crystals had a m. p. of 172-173°.

Found %: N 7.71. $C_{23}H_{18}O_3N_2$. Calculated %: N 7.57.

N-(o-Tolylglycyl)-1-aminoanthraquinone (III). The bath temperature was raised to 125-127°. The heating time was prolonged to 1 hour and 15 minutes. The product was recrystallized from isoamyl alcohol. The orange rectangular prisms had a m. p. of 185-186°.

Found %: N 7.81. $C_{23}H_{18}O_3N_2$. Calculated %: N 7.57.

N-(p-Methoxyphenylglycyl)-1-aminoanthraquinone (VIII). The product was recrystallized from aniline. The prismatic crystals were red with a m. p. of 207-208°.

Found %: N 7.46. $C_{23}H_{18}O_4N_2$. Calculated %: N 7.25.

N-(m-Methoxyphenylglycyl)-1-aminoanthraquinone (VII). The product was recrystallized from toluene. The cubic crystals were red with a m. p. of 146.5-147.0°.

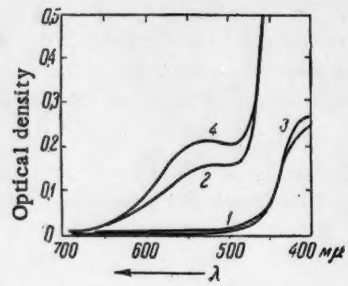
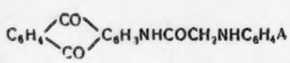



Fig. 2. Absorption curves of α-aminoanthraquinone derivatives of the type:



(in pyridine, $l$ = 0.1 cm). 1) A = H, C = $0.5 \cdot 10^{-3}$M, 2) A = H, C = $0.5 \cdot 10^{-2}$M, 3) A = p-$OCH_3$, C = $0.5 \cdot 10^{-3}$M, 4) A = p-$OCH_3$, C = $0.5 \cdot 10^{-2}$M.

Found %: N 7.39. $C_{23}H_{18}O_4N_2$. Calculated %: N 7.25.

N-(o-Methoxyphenylglycyl)-1-aminoanthraquinone (VI). The product was twice recrystallized from toluene. The elongated rectangular plates were red with a m. p. of 196-197°.

Found %: N 7.43. $C_{23}H_{18}O_4N_2$. Calculated %: N 7.25.

N-(Phenylglycyl)-1-aminoanthraquinone (II). After recrystallization from aniline, the prismatic crystals were light red with a m. p. of 116-117°.

Found %: N 7.91. $C_{22}H_{16}O_3N_2$. Calculated %: N 7.87.

N-(α-Napthylglycyl)-1-aminoanthraquinone (IV). The product was recrystallized from toluene. The violet-red, wedge-shaped crystals had a m. p. of 239-240°.

Found %: N 6.27. $C_{26}H_{18}O_3N_2$. Calculated %: N 6.09.

N-(β-Naphthylglycyl)-1-aminoanthraquinone (X). The product was recrystallized from pyridine. The dark-red, prismatic crystals had a m. p. of 234.5-235.0°.

Found %: N 6.21. $C_{26}H_{18}O_3N_2$. Calculated %: N 6.09.

As a rule, the synthesized compounds were rather readily soluble in pyridine, less so in toluene, chlorobenzene and dichloroethane, still less soluble in benzene and acetone, and difficultly soluble in alcohol.

## LITERATURE CITED


[1] R. E. Schmidt, Zs. angew. Chem. 41, 41 (1928).

[2] J. Houben, Das Antracen und die Antrachinone, Leipzig, 1929.

[3] E. Barnett, Antracene and Antraquinone, London, 1921.

[4] J. Formaneck, Untersuchung und Nachweisorgan. Farbstoffe auf spektroskopischen Wege, 1908, S. 203.

[5] R. A. Morton and W. T. Earlam, J. Chem. Soc. 1941, 159.

[6] C. J. P. Spruit, Rec. trav. chim. 68, 325 (1949).

[7] R. H. Peters and H. H. Sumner, J. Chem. Soc. 1953, 2101.

[8] K. Lauer and M. Horio, J. prakt. Chem. 145, 273 (1936).

[9] E. A. Smirnov, Collection of Articles on General Chemistry, 2, Izd. AN SSSR, 1953, p. 1934;* J. Gen. Chem. 27, 2682 (1957).**

[10] E. A. Smirnov, Proc. Acad. Sci. USSR, 120, No. 3 (1958).**

[11] V. A. Izmail'skii, Reports of the 8th Conference on the Chemistry and Technology of Aniline Dyes, 1950, p. 91.*


* In Russian.

** Original Russian pagination. See C. B. Translation.

[12] V. A. Izmail'skii and P. A. Solodkov, Proc. Acad. Sci. USSR, 60, 587 (1948).

[13] V. A. Izmail'skii and E. A. Smirnov, J. Gen. Chem. 25, 1400 (1955).*

[14] Bayer, Ger. Pat. 213960; Chem. Zbl. 2, 1286 (1909).

M. I. Gubkin Moscow
Petroleum Institute

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# ACYLATION OF A SERIES OF AROMATIC COMPOUNDS IN THE PRESENCE OF METALS

I. P. Tsukervanik

(Presented by Academician A. A. Balandin, February 5, 1958)

In some old publications related to Zincke's studies of reactions, there are described a number of attempts to acylate aromatic hydrocarbons with acyl chlorides in the presence of zinc dust and iron [1-4]. Good results were obtained only in the benzoylation of naphthalene. A recent patent [5] proposes this reaction for the synthesis of 1,5-dibenzoylnaphthalene.

However, it should be noted that benzoylation of naphthalene, biphenyl, and anthracene takes place rather readily without a catalyst as a thermal reaction [6].

Indian authors, studying the activity of metals (uranium, cerium, titanium, and chromium) in various condensation reactions, obtained small yields of ketones from acetyl chloride and benzoyl chloride and benzene [7].

Through experiments based on our work on homolytic acylation of aromatic rings [8-10], we have confirmed that it is possible to carry out acylations in the presence of various metals. In these experiments, which were carried out in a flask fitted with reflux condenser, a mixture of the acyl chloride and the aromatic compound was heated (90-150°) with powdered copper, tungsten, or molybdenum; 0.05-0.01 gram-atom of the metal was used for each mole of acyl chloride. The condensation was accompanied by considerable evolution of hydrogen chloride, which ceased after 4-16 hours (simultaneously, the acyl chloride in the mixture disappeared).

The mixture was decanted from the catalyst, and, after a water wash, it was fractionated. When copper was used, a certain amount of $Cu_2Cl_2$ was formed; the other metals were not changed appreciably, and could be used in further experiments.

Under a given set of conditions, the results of the acylation depend on the boiling point of the acyl chloride and the mobility of the hydrogens of the aromatic ring. The benzoylation of anisole and m-xylene proceeded the most readily, the yield of ketones being close to theoretical. Control experiments in which the benzoylation was carried out under the same conditions without a catalyst failed to yield any ketones.

Toluene gave 50% p-methylbenzophenone, benzene gave 20% benzophenone, and chlorobenzene gave only traces of ketone. Much unreacted benzoyl chloride was recovered in the last three reactions.

Attempted acetylations of benzene and toluene were unsuccessful, but m-xylene gave 20% 2,4-dimethylacetophenone, and anisole gave 30% 4-methoxybenzophenone. The reaction proceeded somewhat better with butyryl chloride and still better with caproyl chloride (60% 4-methoxycaprophenone). It is evident that other conditions must be selected for reactions with low-boiling acyl chlorides.

We believe that the present method of acylation of aromatic compounds possesses advantages in comparison with reactions in the presence of aluminum chloride.

The results of several reactions are presented in Table 1. The physical constants of the substances and of their derivatives, also presented in the table, are in agreement with the literature values.

TABLE 1

| Reagents | Catalyst | Temperature °C | Heating time, hours | Main reaction product | Yield %, of theoretical: overall | Yield %, of theoretical: based on reacted acyl chloride | B. p., °C/mm Hg | M. p. °C | Derivative (m. p.) |
|---|---|---|---|---|---|---|---|---|---|
| Benzoyl chloride, benzene | Copper | 90 | 15 | Benzophenone | 20 | 60 | 156—158/10 | 46—47 | Oxime (141-142°) |
| Benzoyl chloride, toluene | Copper, molybdenum | 110—120 | 16 | 4-Methylbenzophenone | 50 | 80 | 164—166/10 | 58 | Semicarbazone (121°) |
| Benzoyl chloride, m-xylene | Molybdenum, tungsten | 120—140 | 4—6 | 2,4-Dimethylbenzophenone | 97 | — | 142—144/4 | — | Dinitro derivative (144°) |
| Benzoyl chloride, anisole | Copper, molybdenum, tungsten | 150<br>90<br>90 | 4<br>8<br>8 | 4-Methoxybenzophenone | 94 | — | 160—162/3 | 60—61 | 2,4-Dinitrophenylhydrazone (178-180°) |
| Caproyl chloride, anisole | Molybdenum | 90 | 10 | 4-Methoxycaprophenone | 60 | 80 | 141—142/5 | 41 | 2,4-Dinitrophenylhydrazone (141°) |
| Butyryl chloride, m-xylene | Copper | 90 | 20 | 2,4-Dimethylbutyrophenone | 30 | 80 | 130—131/13 | — | 2,4-Dinitrophenylhydrazone (169°) |
| Butyryl chloride, anisole | Molybdenum, copper | 90 | 8<br>20 | 4-Methoxybutyrophenone | 45 | 80 | 159—160/20 | — | Semicarbazone (183°) |
| Acetyl chloride, m-xylene | Molybdenum | 90 | 10 | 2,4-Dimethylacetophenone | 20 | — | 104—106/10 | — | Semicarbazone (185-186°) |
| Acetyl chloride, anisole | Copper | 90 | 10 | 4-Methoxyacetophenone | 30 | -- | 130—132/12 | 38 | Semicarbazone (195-196°) |

## SUMMARY

1. The acylation of an aromatic ring with acyl chlorides in the presence of powdered copper, molybdenum, or tungsten was shown to be possible.

2. The following yields were obtained: 4-methoxybenzophenone (95%), 2,4-dimethylbenzophenone (97%), 4-methoxycaprophenone (60%).


## LITERATURE CITED


[1] T. Zincke, Ber. 6, 137 (1873).

[2] S. Grucarevic and V. Merz, Ber. 6, 1238 (1873).

[3] K. Elbs and G. Steinike, Ber. 19, 1965 (1886).

[4] O. Kegel, Lieb. Ann. 247, 178 (1888).

[5] Patent of the FRG [Federal Republic of Germany] No. 941,123; Ref. J. Chem. 2155 (1957).

[6] C. Nenitzescu, D. Isacescu and C. Ionescu, Lieb. Ann. 491, 210 (1931).

[7] V. Sharma and S. Dutt, Chem. Zbl. 2, 966 (1936); L. Lal and S. Dutt, J. Ind. Chem. Soc. 9, 565 (1932); 12, 389 (1935); 5, 513 (1928).

[8] I. P. Tsukervanik and S. G. Mel'kanovitskaia, J. Gen. Chem. 27, 885 (1957).*

[9] I. P. Tsukervanik and G. S. Semeshko, J. Gen. Chem. 27, 1143 (1957).*

[10] S. G. Mel'kanovitskaia and I. P. Tsukervanik, Bull. Acad. Sci. UzbSSR, Ser. Chem. Sci. No. 3, 51 (1957).



V. I. Lenin Central Asiatic
State University



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# THE USE OF FRONTAL ANALYSIS IN GAS-LIQUID CHROMATOGRAPHY OF RADIOACTIVE AND NONRADIOACTIVE GASES

M. I. Ianovskii and G. A. Gasiev

(Presented by Academician S. I. Vol'fkovich, January 2, 1958)

Gas-adsorption frontal analysis has not found widespread use in analytical practice in view of the fact that in this method the dynamics of adsorption in a layer of adsorbent is complicated by displacement processes associated with the mutual effect of the components of the mixture during their adsorption on the surface [1-3], whence it is impossible to determine the composition of the mixture directly from a frontal diagram. The calculations require exhaustive data on the adsorption isotherms of the mixtures and individual components over the entire concentration range studied. The insufficient development of the theory of adsorption of mixtures under static and dynamic conditions and the insufficiency of experimental material in this field limit the application of adsorption frontal analysis to a narrow range of systems which obey an adsorption equation of the Langmuir type [2, 3].

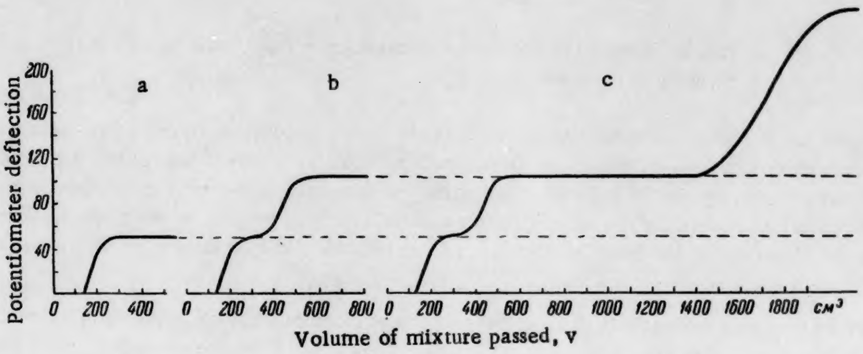


Fig. 1. Frontal effluent curves of hydrocarbon gases. a) 0.98% $C_3H_6$ in hydrogen; b) 0.98% $C_3H_6$ and 1.03% $C_4H_6$; c) 0.98% $C_3H_6$, 1.03% $C_4H_6$, and 2.93% n-$C_6H_{14}$.

In the present work, an attempt was made to use frontal analysis in gas-liquid chromatography, the development variant of which became widely used after the well-known work of James and Martin [4].

As is well known, under specific conditions of gas-liquid chromatography (low concentrations, low solubility of the gas in the liquid), it is possible to disregard the difference between the solubility of a gas in a mixture and the solubility of the pure gas. This is permissible owing to the absence of the mutual effect of the components in the gaseous and liquid phases; this considerably simplifies frontal analysis, and permits the determination of the composition of the mixture being analyzed without resorting to preliminary measurements and calculations — i.e., directly from the frontal diagram.

The experiments consisted of passing the mixture of substances being analyzed continuously through the column and taking the so-called frontal diagram, which characterizes the relationship between the concentrations of components at the effluent end of the column and the volume of mixture passed through it. The basic elements of the experimental apparatus were a gas-liquid chromatographic column, which was filled with a specially treated inert packing (diatomaceous earth) impregnated with a high-boiling liquid (nitrobenzene, dibutyl phthalate, etc.), and a thermal conductivity gas analyzer with an EPP-09 recording potentiometer.

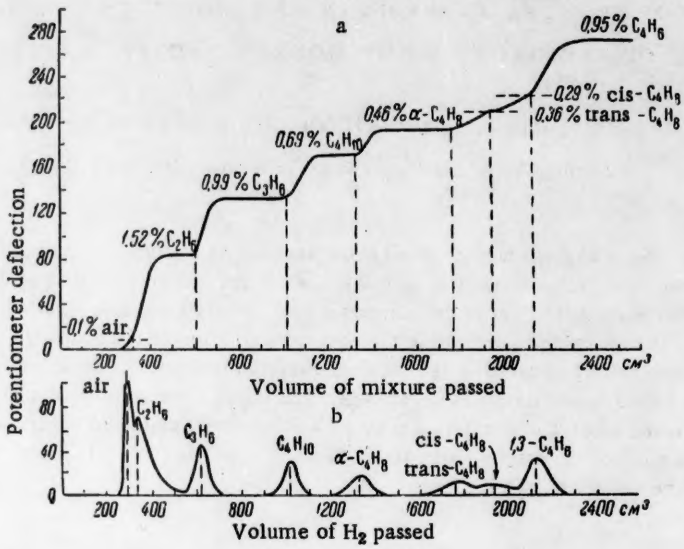


Fig. 2. Frontal (a) and development (b) gas-liquid analysis of multicomponent mixtures.

In Fig. 1 are presented some frontal diagrams taken with a gas-liquid column (diatomaceous earth + dibutyl phthalate; length 1.65 m, d = 5 mm; flow rate 7 ml/minute). They indicate that it is possible, to a first approximation, to neglect the mutual effect of the components in the stationary phase; the beginning of the $C_3H_6$ step and its height show the same propylene content (0.98%) on each of the three diagrams in spite of the addition of butadiene and hexane. Hexane, in turn, has no effect on the height of the butadiene step (compare Figs. 1b and 1c).

Figure 2 illustrates the analysis of an eight-component mixture (diatomaceous earth + nitrobenzene; length 16 m, d = 5 mm; flow rate 7 ml/minute). In Fig. 2b is shown a development gas-liquid chromatogram of 50 cc of a mixture of the same composition as the mixture used in the experiment represented by Fig. 2a; the chromatogram was obtained under the same conditions as were used for the frontal diagram (column length, carrier gas rate, accuracy of detection). A comparison of Figs. 2a and 2b shows that each step on the frontal diagram corresponds to a development peak.

Frontal gas-liquid analysis can be used along with the radiochromatographic development method [5] for the rapid determination of the specific radioactivity of the components of a gas mixture. For this purpose, the gas mixture is passed through a radiometric detector, which is in parallel with (or subsequent to) the conductivity gas analyzer; the construction of the radiometric detector was described earlier [6]. The radiometric detector, into which is built a thin-walled end-window counter which is connected in parallel into the integrating circuit of a counting rate meter, permits the determination of the radioactivity of the gas stream at the effluent end of the column. The readings of the radiometric detector are recorded simultaneously with the readings of the thermal conductivity cell of the gas analyzer on a single strip chart.

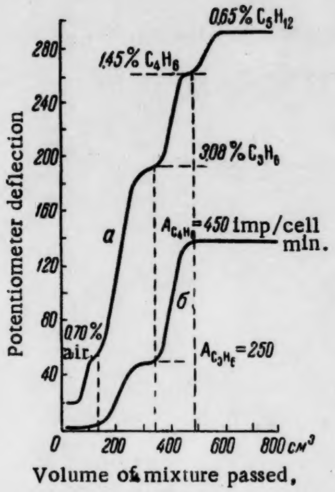


Fig. 3. Frontal gas-liquid radiochromatogram. a) Recordings of the readings of the thermal conductivity gas analyzer, b) recording of the readings of the radiometric detector.

A typical frontal gas-liquid radiochromatogram of a mixture of air, propylene, butadiene, and pentane in hydrogen is shown in Fig. 3 (diatomaceous earth + dibutyl phthalate; length of column 1.65 m d = 5 mm; gas rate 7 ml/minute). It shows that only two of the four components are radioactive ($C_3H_6$ and $C_4H_6$), since only for the propylene and butadiene steps on Curve a are there corresponding steps on Curve b. The specific radioactivity of the $i^{th}$ component, $I_{spi}$, is readily determined as the ratio of the height of the step, $\Delta I_i$, on Curve b to the height of the $\Delta C_i$ step on Curve a:

$$I_{spi} = \frac{\Delta I_i}{\Delta C_i},$$

these values being obtained from specific scales. At the conclusion of the analysis, when no more new steps are registered on the frontal diagram, the column is desorbed; carrier gas ($H_2$) is passed through it at the same rate until a stable null reading is reached. This purging process can be used to record a desorption frontal diagram, which is also sometimes used to determine the composition of a mixture. The solid line ABCDE in Fig. 4 is a frontal diagram for a mixture of propylene and butadiene. At point E, which corresponds to the time at which feeding of the mixture of $C_3H_6$ and $C_4H_6$ to the column was stopped, passage of hydrogen into the column was started. The resulting desorption curve A'B'C'D'E' is identical with the frontal diagram ABCDE, and can be combined with it by transposing the curve EA'B'C'D' at the point 0 so that the v axis coincides with the v' axis. The transposed curve A"B"C"D"E" is the mirror image of the frontal curve ABCDE. At the conclusion of the desorption experiment, the column is again ready to take a chromatogram.

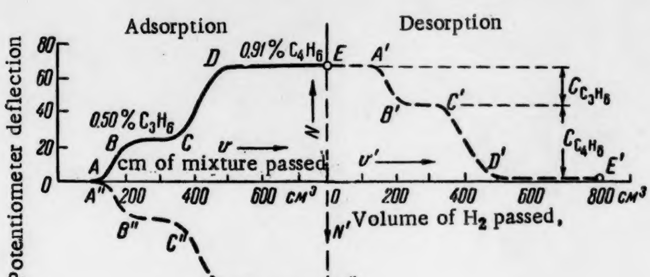


Fig. 4. Adsorption and desorption frontal diagrams of mixtures of propylene and butadiene.

## LITERATURE CITED

[1] M. M. Dubinin and S. Iavich, J. Appl. Chem. 9, 1191 (1936).

[2] O. M. Todes, J. Appl. Chem. 18, 591 (1945).

[3] S. Claesson, Adsorption Analysis of Mixtures,* 1950.

[4] A. T. James and A. J. P. Martin, Biochem. J. 56, 679 (1952).

[5] M. I. Ianovskii, D. S. Kapustin and V. A. Nogotkov-Riutin, Isotopes in Catalysis,* 9, 1957.

[6] M. I. Ianovskii, Radiochromatography, Instruments and Installations,* Moscow, 1958.

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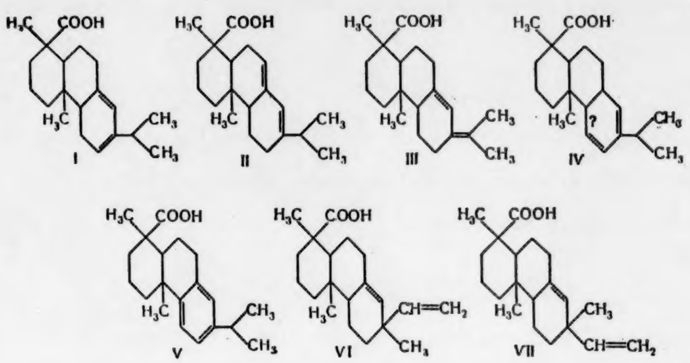
# ISODEXTROPIMARIC ACID – A COMPONENT OF THE RESIN ACIDS OF THE OLEORESIN OF THE SIBERIAN CEDAR – PINUS SIBIRICA (RUPR) MAYR.

I. I. Bardyshev and Kh. A. Cherches

(Presented by Academician B. A. Arbuzov, December 30, 1957)

Systematic studies of the resin acids of the oleoresins of conifers have been carried out by V. V. Shkatelov [1] and B. A. Arbuzov [2].

The following resin acids have been found in the oleoresins of various native conifers: levopimaric (I) [3, 4], abietic (II) [5, 6], neoabietic (III) [7], palustric (IV) [8, 9], dehydroabietic (V) [9], and dextropimaric (VI) [3,4]. $\alpha$- and $\beta$-Sapinic acids, which were formerly considered basic components of the acid part of the oleoresins of the common pine [3] and the common fir [4, 10], have been shown to be not individual acids, but mixtures of such acids as levopimaric, abietic, neoabietic, palustric, and dextropimaric acids [8].



Isodextropimaric acid (VII), which is distinguished from dextropimaric acid (VI) only by the different steric positions of the substituents at $C_7$, was first isolated from the oleoresin of the American long-leaf pine Pinus palustris [11], but up to the present it had not been found in the balsams of native conifers.

The present investigation showed that isodextropimaric acid, along with abietic acid [12], is a component of the acid part of the oleoresin of the Siberian cedar.

## EXPERIMENTAL

The oleoresin was collected from a stand of Siberian cedar in the Gorno-Altai Autonomous Region. The trees were tapped by the downward cut method. The oleoresin collected in the receiver over a period of 4-7 days. The oleoresin contained 18% turpentine. The resin acids of the oleoresin were converted to the sodium salts. The neutral material was removed from the solution of the salts by repeated extraction with ether. The salts were decomposed with a 0.5% aqueous solution of acetic acid, and the resin acids were obtained after the usual treatment (Fig. 1, 1); m. p. 66-70° and $[\alpha]_D = 26.5°$ (all specific rotations were determined with 1% solutions in ethanol).

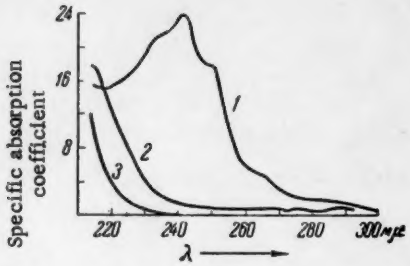



Fig. 1. Ultraviolet absorption spectra: 1) original resin acids, 2) resin acids after treatment with maleic anhydride, 3) isodextropimaric acid.

Fig. 2. Crystals of isodextropimaric acid obtained by recrystallization of the acid from ethyl acetate.

The resin acids (106 g) were dissolved in kerosene (b. p. 160-180°) and treated with maleic anhydride at 145-150° for 20 hours. The reaction product was dissolved in a 2% aqueous solution of sodium hydroxide, the neutral material was extracted with ether, and the salts were acidified to a pH of 6.2 by adding crystalling boric acid to the solution. This procedure resulted in 20 g of resin acids (Fig. 1, 2) with a m. p. of 65-73°, $[\alpha]_D = +24.1°$. The resulting acids were converted by the usual method to the bornylamine salts, which, after two recrystallizations from alcohol, melted at 178-180° and had $[\alpha]_D = 0.0°$. The bornylamine salts were decomposed with boric acid. Isodextropimaric acid, m. p. 162-164°, was isolated from the thus obtained resin acids (m. p. 152-156°) by three recrystallizations from acetic acid. The elemental analysis, neutralization number, and ultraviolet spectrum (Fig. 1, 3) were in complete agreement with those of isodextropimaric acid. The methyl ester of isodextropimaric acid, prepared by treating the latter with diazomethane, had its characteristic m. p. of 61-62°.

## LITERATURE CITED


[1] V. V. Shkatelov, The Composition of the Solid Fraction of Natural Resins and Colophonies, 1939.*

[2] B. A. Arbuzov, Bull. Acad. Sci. BSSR, Div. Chem. Sci. No. 2 (1940).

[3] V. N. Krestinskii, S. S. Malevskaia, N. F. Komshilov and E. V. Kazeeva, J. Appl. Chem. 12, 1939 (1939).

[4] S. S. Malevskaia and S. D. Kharad, J. Appl. Chem. 23, 153 (1950).**

[5] I. I. Bardyshev and L. I. Ukhova, Proc. Acad. Sci. USSR, 109, 89 (1956).**

[6] I. I. Bardyshev and Kh. A. Cherches, J. Appl. Chem. 29, 1888 (1956).**

[7] I. I. Bardyshev, V. V. Kokhomskaia and L. I. Ukhova, Proc. Acad. Sci. USSR, 112, 653 (1957).**

[8] I. I. Bardyshev, L. I. Ukhova, et al., Thesis Reports of the All-Union Conference on the Chemistry of Plant Materials, Tashkent, 1956.*

[9] I. I. Bardyshev and Kh. A. Cherches, Proc. Acad. Sci. USSR, 116, No. 6 (1957).**

[10] S. S. Malevskaia, J. Appl. Chem. 30, 903 (1957).**

[11] G. C. Harris and T. F. Sanderson, J. Am. Chem. Soc. 70, 2079 (1948).

[12] A. P. Pentegov and I. V. Pentegova, Trans. Chem.-Met. Inst. Western Siberian Affiliate Acad. Sci. USSR, No. 7 (1953).


* In Russian.

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Institute of Chemistry
Academy of Sciences BSSR



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CONSTRUCTION OF CONODES IN TWO-PHASE REGIONS OF STRUCTURAL DIAGRAMS OF METALLIC SYSTEMS BY A MICROHARDNESS METHOD

V. N. Vigdorovich

(Presented by Academician A. A. Bochvar, February 8, 1958)

The determination of the position of a conode in two-phase regions of structural diagrams is one of the most laborious operations in physicochemical analysis, especially during investigations of metallic systems in the solid state. Such a determination requires a knowledge of the chemical composition of the individual phases, and this constitutes the principal difficulty. However, using the microhardness method, it is possible to manage a solution to this problem.

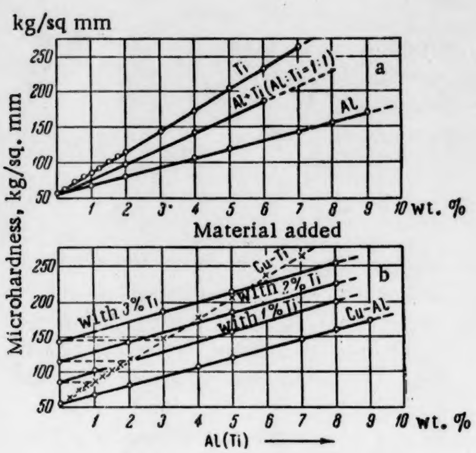


Fig. 1. Additivity of increments of microhardness of a three-component solid solution with respect to incremental changes in microhardness in the corresponding two-component systems. The geometrical construction emphasizes the fact that a change in microhardness with composition for sections of the structural diagram of copper–aluminum–titanium at constant titanium content parallels its change in the system copper–aluminum, and is shifted by a specific amount corresponding to the titanium content in the alloys.

In work carried out previously [1, 2], it was shown that the nature of the experimentally determined microhardness isotherms for various sections of three-component structural diagrams depends on the orientation of the sections investigated with respect to the conode. The present communication assumes the task of demonstrating the feasibility of using such changes in microhardness for the determination of the fixed position of the conode.

In the majority of cases of the formation of binary solid solutions in metallic systems, the increase in microhardness of the solid solution is proportional to its concentration.* Without any appreciable deviations, an analogous relationship frequently holds for ternary solid solutions (Fig. 1a). In confirmation of these positions, which were expressed in reference [3], an increment of microhardness in a ternary solid solution in the system copper–aluminum–titanium** also shows up as an additive property of the microhardness in the corresponding binary solid solutions. An illustration of this property based on experimental data obtained by a specially developed method [4], is presented in Figs. 1a and 1b.

This relationship between the microhardness of a solid solution and concentration can be used to determine the position of the conode. Since any given value of the microhardness may relate to a series of solid solutions, it is additionally necessary to make use of one of the properties of conjugate points of the conode.

*Generally speaking, the indicated dependence of microhardness of solid solutions can be represented as a curve convex from the concentration axis. However, the curvature of this curve is insignificant if the concentrations are not too high. Therefore, in the case of a limited solid solution – the more so, if it is small – this assumption is fulfilled rather well and linearity is retained almost until the limiting concentration is reached.

**The experimental data on this system are presented here as an example.

These points must lie on a surface of limited solubility. Consequently, considering this circumstance, it will be easy to find the concentration from the known value of the microhardness. It is simplest to use geometrical construction for this purpose. In Fig. 2, the required construction is carried out for an example in which the position of the conode is determined in the region of $\alpha + Cu_3Ti$ on the structural diagram of the system copper—aluminum—titanium at temperatures of 500 and 850°.

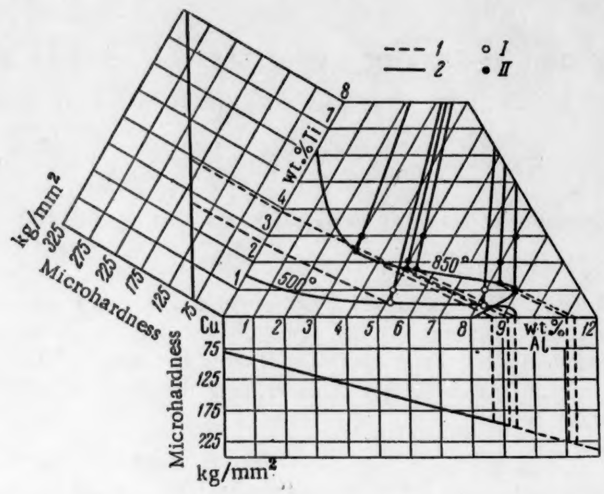


Fig. 2. Construction of the conode in the region $\alpha + Cu_3Ti$ of the structural diagram for copper-aluminum—titanium at temperatures of 500 and 850° from data obtained by microhardness measurements. 1) Isoscleres, 2) solubility isotherms; I) 500°, II) 850°.

At the start, the following data are required for carrying out such constructions.

First, it is necessary to know the dependence of microhardness of the solid solution on concentration in the corresponding two-component systems. If these relationships are linear and there is experimental confirmation of the additivity of microhardness increments of the three-component solid solution, then the dependence of microhardness on concentration is expressed as a plane having a general location such that it passes through the straight lines expressing the dependence of the microhardness in the corresponding two-component systems and such that the slope with respect to the concentration axes of both alloying components is determined by the amount of hardening caused by one or the other component during solution. In connection with this, it is possible to confine oneself to the value of the dependence of microhardness on concentration for one of the two-component systems (either of the two variants can be used) and also to the value of the ratio of the hardening of the solid solution observed during the solution of one component to the hardening of the solid solution during solution of the other component.

Second, it is necessary to study the common solubility of both components at those temperatures for which the position of the conode is being determined.*

Third, it is necessary to have data from measurements of the microhardness of the solid solution in the two-phase region in which the position of the conode is being investigated. The investigation is carried out on annealed samples. The results of the measurements must relate to such a content of components in the alloy that microheterogenization of the crystals of the solid solution will have no effect on the value of the microhardness [1, 5-10]. For this purpose, an alloy is selected through which the desired conode must pass and which

*It should be noted that not all points of a plane having a general position reflecting the dependence of the microhardness of the solid solution on concentration will correspond to actually realizable values. In a projection onto plane of the concentration triangle, the region of points having specific physical meanings for equilibrium solid solutions will be limited to the solubility isotherm.

is located as close as possible to the solubility isotherm. It is possible to remove this limitation by subjecting the alloys, prior to the investigation of their microhardness, to a lengthy homogenization which is sufficient to eliminate microheterogenization of the crystals of the solid solution [1, 10, 11]. In this case, if the position of the conode is determined in two-phase regions located between the liquidus and solidus surfaces, hardening of the alloys is possible only out of the region of the solid-liquid state, which is limited by the surface of the beginning of linear shrinkage [11-13].

Then, from the known, measured values of the microhardness of the solid solution of the alloy in the two-phase region, lines of equal values of microhardness (isoscleres) are drawn. It is obvious that all isoscleres in a given three-component system will be parallel. Therefore, the first requirement for drawing isoscleres is the determination of this direction. For this purpose, in the case of the system copper—aluminum—titanium, for example, it is possible to make use of the known values of the hardening connected with the formation of solid solutions in the systems copper—titanium and copper—aluminum. Solution of titanium in copper causes greater hardening than does solution of aluminum in copper. Experiments have shown that the microhardness increases by 33 kg/sq. mm upon the introduction of 1% titanium into the solid solution and by 12.4 kg /sq. mm upon the introduction of 1% aluminum. Therefore, with equal scales on the axes, the isoscleres in the system copper—aluminum—titanium intersect the concentration axis in the copper—aluminum system at intercepts which are 2.66 times greater than the intercepts of the isoscleres on the concentration axis in the copper—titanium axis (33.0 : 12.4 = 2.66). After the direction of the isoscleres has been established, for drawing the isoscleres from the given values of the microhardness it is possible to make use of the relationship between microhardness and concentration in any of the two-component systems. In Fig. 2 is shown the construction of the conode at 500° from the known dependence of microhardness on concentration in the copper—titanium system and at 850° from this same relationship in the copper—aluminum system.

The isosclere is drawn to the intersection with the corresponding solubility isotherm. The point of intersection represents the point on the concentration triangle which corresponds to the limiting saturated solution having a microhardness and, consequently, a concentration which are the same as those of the solid solution of the selected alloy in the two-phase region.

Then, by joining the points of intersection of the isoscleres with the corresponding solubility isotherms and the points representing the compositions of the alloy for which the measurements of the microhardness of the solid solution were carried out, we obtain the direction of one of the conodes at the given temperature. All such points are denoted on Fig. 2 by circles.

If the isosclere meets the solubility isotherm in several points, it then becomes necessary to select one of several variants. One must then be guided by data obtained during those geometrical constructions which led to unequivocal solutions. Moreover, sometimes certain known data on the possible position of the second conjugate point of the conode facilitate the solution of this problem. Thus, for example, in the system copper-aluminum—titanium there are apparently formed limited solid solutions based on the binary intermetallic compound $Cu_3Ti$, and continuations of the conodes intersect close to the ordinates of this compound.

Under favorable conditions, the position of a conode can be plotted very accurately. For example, accuracy in the construction of a conode is provided by a small specific volume of the second phase which heterogenizes the solid solution as compared to the specific volume of the solid solution, when there is a possibility of selecting for the determination of the microhardness an alloy lying in the two-phase region far from the solubility isotherm [10]. The case where the angle at which the isosclere intersects the solubility isotherm is close to a right angle is also favorable. If, moreover, in the direction of the conode there are other alloys whose solid solutions do not undergo microheterogenization thereby affecting the microhardness, then it is possible to check the construction which has been carried out and to make it more precise.

All of the enumerated data required for the determination of the position of the conode are usually available after carrying out an investigation of the variation in microhardness with composition *, and the construction of the conode in this case can be merely a concluding operation.

In conclusion, we should mention the possibility of using the microhardness method for the construction of conodes in three-component systems in which the solid solutions do not possess the indicated properties of linearity and additivity. For this purpose, it is necessary to establish first of all the dependence of the micro-

* The results of the investigation of the system copper—aluminum—titanium are reported in references [14, 15].

hardness over the entire length of the solubility isotherm, or over that portion which is of specific interest, by direct measurement, as far as possible, on a large number of alloys. Then, from the known value of the microhardness of the alloy in the two-phase region and from the established dependence, the location of the alloy with equal hardness is determined on the solubility isotherm by interpolation. The location of this alloy corresponds to the location on the diagram of one of the conjugate points of the conode. In order to construct the conode, it then remains to connect this point with the point of the alloy of the two-phase region for which the microhardness determination was carried out.

## LITERATURE CITED


[1] V. M. Glazov, V. N. Vigdorovich and G. A. Korol'kov, J. Phys. Chem. 31, No. 8, 1891 (1957).

[2] V. M. Glazov and N. N. Glagoleva, Factory Labs., 23, No. 12, 1481 (1957).

[3] N. N. Glagoleva and V. M. Glazov, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 1, 130 (1958).*

[4] V. N. Vigdorovich and V. M. Glazov, Bull. of Institutions of Higher Education, Ministry of Higher Education SSSR, Nonferrous Metallurgy, No. 3 (1958).

[5] V. M. Glazov, V. N. Vigdorovich and G. A. Korol'kov, Factory Labs. 22, No. 11, 1343 (1956).

[6] A. A. Bochvar and O. S. Zhadaeva, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 10-11, 108 (1945).

[7] A. A. Bochvar, Collection Scientific Works of the Moscow Institute of Nonferrous Metals and Gold, No. 18 (1947).**

[8] A. M. Korol'kov and E. S. Kadaner, Proc. Acad. Sci. USSR, 74, 120 (1950).

[9] A. M. Korol'kov and E. S. Kadaner, Reports of the Conf. on Microhardness, 1951.**

[10] V. M. Glazov, V. N. Vigdorovich and G. A. Korol'kov, Coll. Technology of Nonferrous Metals, No. 29 (1958). **

[11] V. M. Glazov and V. N. Vigdorovich, Coll. J. No. 4 (1958).*

[12] A. A. Bochvar and V. I. Dobatkin, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 1-2 (1945).

[13] I. I. Novikov, Scientific Works of the Students of the Moscow Mining-Metallurgical Institute**, 1949, p. 131.

[14] A. A. Bochvar and I. I. Novikov, Coll. Technology of Nonferrous Metals**, No. 23 (1952).

[15] V. N. Vigdorovich, A. N. Krestovnikov and M. V. Mal'tsev, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 2 (1958).*

[16] V. N. Vigdorovich, A. N. Krestovnikov and M. V. Mal'tsev, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 3 (1958).*



M. I. Kalinin Moscow Institute
of Nonferrous Metals and Gold



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## SOLID SOLUTIONS IN THE SYSTEM AlSb – GaSb

N. A. Goriunova and I. I. Burdiian

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The initial binary substances of the pseudobinary section AlSb-GaSb of the ternary system Al–Sb–Ga are semiconductors of the type $A^{III}B^{V}$; a considerable amount of literature has been devoted to the properties of these materials up to the present. The possibility of the formation of homogeneous regions in alloys of substances of this type is of interest from the point of view of the preparation of semiconductors with a more suitable combination of electrical and physical properties for practical purposes than occurs in the binary compounds.

According to the data of Köster and Thoma [1], who investigated the system AlSb–GaSb as well as the systems AlSb–InSb and GaSb–InSb, the binary components of these systems exhibit no appreciable mutual solubility in the solid state, and the systems are treated as eutectic systems.

One of the authors of the present paper, together with N. N. Fedorova and I. E. Gorshkov, studied the system GaSb–InSb and also tentatively investigated the system AlSb–InSb [2, 3]. In contradistinction to the data of Köster and Thoma, mutual solubility of the binary components was observed in these systems over a broad concentration interval. This work provides an explanation of a basic peculiarity of these systems, the presence of a tendency toward the formation of nonequilibrium states in connection with the covalent type of interaction between the atoms of these substances.

Apparently, the latter circumstance was not taken into consideration by Köster and Thoma, and this led them to the erroneous conclusion that solid solutions are not present in the systems AlSb–InSb and GaSb–InSb. As regards the system AlSb–GaSb, as a result of preliminary experiments it has been proposed by one of the present authors that solid solutions exist in this system.

In the present paper, the results of a physicochemical investigation are presented in confirmation of this proposal.

The substances under investigation were prepared by fusion of the original simple substances in graphite crucibles in an atmosphere of argon. Just as in the work of Köster and Thoma, alloys were prepared with ratios of the original binary components 1:4, 1:1, and 4:1, and also the compounds gallium antimonide and aluminum antimonide. The following methods were used to investigate the nature of the interaction of the substances in these alloys: thermal analysis, investigation of the microstructure and microhardness, and investigation of the distribution of electrical conductivity along the bar. The x-ray method was not used, since preliminary experiments showed that this method was not effective owing to the very close lattice periods of these compounds.

The thermal analysis was carried out with a Kurnakov pyrometer. About 7 g of the substance was fused in evacuated quartz Stepanov tubes. The rate of heating and cooling in these experiments was 10-15° per minute. Both the simple curves and the differential curves were taken.

The microhardness was determined with a PMT-3 apparatus; the surface of the samples was first etched with a 5% solution of ferric chloride in hydrochloric acid in a ratio of 1:2.

The distribution of electrical conductivity along the bar was determined by the usual probe method.

The investigation of the substances carried out immediately after synthesis showed that their compositions were clearly heterogeneous. Thus, the heating and cooling curves gave results in agreement with those of Köster and Thoma. The structure of the substances was finely crystalline, and the microhardness values were considerably scattered, both within the grains and between them.

The electrical conductivity values were also considerably scattered along the bar.

Lengthy annealing of the substances in powdered form at temperatures close to the melting point of the low-melting binary component was used in the previous work [2, 3] to homogenize the GaSb–InSb alloys. In addition to being lengthy, this method had still another disadvantage; the substance could not be used in the powdered form for the investigation of the electrical properties nor for the manufacture of a specific type of semiconductor apparatus. Therefore, in the initial period of the investigation, the alloys were homogenized by annealing the bars, in the form of pieces, under vacuum at a temperature of 600° for 2000 hours. However, the annealing did not yield particularly good results.

Later, the alloys were homogenized by another method, namely, equalization by zone melting. We selected this method owing to the following considerations: a substance of the type $A^{III}B^{V}$ is, by nature, very close to semiconductors – elements of Group IV; therefore, we assumed that alloys of the type $A^{III}B^{V} - A^{III}B^{V}$ could be homogenized by the same method as alloys of silicon and germanium [5].

Equalization by zone melting was carried out by the usual method, by moving the heater alternately in reverse directions at a rate of 9-10 mm/hour, the initial length of the entire bar being 25 cm and the breadth of the molten zone 3-4 cm. The temperature in the molten zone corresponded to the temperature on the liquidus diagram of Köster and Thoma [1]. After twenty passes of the zone, the central part of the bar, 6-8 cm in length, was subjected to investigation.

A study of the microstructure of the samples showed that they were coarsely crystalline with grain sizes up to 1 mm and that they did not have any inclusions (of eutectic or other nature). Scattering of the microhardness values and of the electrical conductivity along the length became considerably less, and the microhardness of the alloys of this system had a maximum at the composition 1 : 1 (AlSb : GaSb).

Before the investigation of the alloys by thermal analysis, they were analyzed chemically at our request by T. V. Cherkashina, to whom the authors express their sincere appreciation. The analyses showed a tendency toward a certain shifting of the more fusible compound in the direction of the movement of the zone. Therefore, the data on composition, cited by us below during a consideration of the results of the thermal analysis, can deviate somewhat on the side of an increase in the amount of the more difficultly fusible compound – aluminum antimonide.

The thermal analysis of the alloys of the system gave results which differed sharply from the data of Köster and Thoma. In Fig. 1 are presented both the data obtained by us and those of the indicated investigators. Our data indicate that in the system investigated, the interaction of the binary components under conditions approximating equilibrium did not have an eutectic character, but led to the formation of solid solutions over a wide concentration interval. This turned out to be a very satisfactory application of zone equalization prior to thermal analysis, and, so far as is known to us, it has not been used by anyone else.

The samples of alloys, after zone melting, were allowed to stand for a long period of time in the air with the aim of qualitatively comparing their behavior with the behavior of aluminum antimonide, which, as is well known, corrodes in air. It developed that with an increase in the content of gallium antimonide in the alloys, they became more stable with respect to the action of air of ordinary humidity. Samples with a gallium antimonide content of more than half were especially stable (no changes in the polished surface were observed over a period of two months).

A more complete investigation of the structural diagram with a greater number of samples is a requirement ment of the future. It is possible that with a more complete homogenization, the solidus line would rise somewhat. Nevertheless, these data unequivocally answer the question of the nature of the interaction of the components in this system; undoubtedly, the formation of solid solutions takes place in the system over a broad concentration interval. Keeping in mind the peculiarities of structure and of type of bonds of the present substances and also the nature of the changes in microhardness, it can be asserted that these solutions are substitutional solid solutions. We believe that the alloys of this system will have practical significance, since the

combination of physicochemical and electrical properties in them is probably considerably more favorable than the combination of these same properties in the original binary compounds.

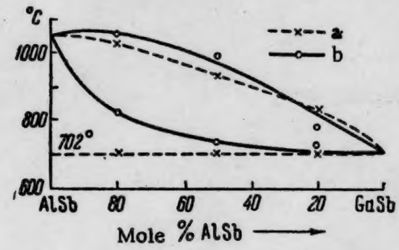


Fig. 1. Quasibinary section AlSb—GaSb: a) According to Köster and Thoma; b) our data.

The fact of the formation of substitutional solid solutions in the pseudobinary section AlSb—GaSb of the ternary system Al—Sb—Ga, together with data on the systems GaSb—InSb and AlSb—InSb, previously investigated [2, 3], permits elimination of the contradiction noted by certain authors [6, 7] in connection with consideration of the data of Köster and Thoma. This contradiction is that in systems of the same type with substitutional components which differ sharply in all characteristics (GaP—GaAs and InP—InAs), substitution occurs, but in the system AlSb—GaSb, where the substituting components are closely similar, substitution does not occur.

Using our data, we find it possible to interpret the formation of substitutional solid solutions in substances of the type $A^{III}B^{V}$ from a single point of view, by comparing the electrical affinity constants of the substituting elements [9].

TABLE 1

| System | Nature of interaction | Elec. affinity constants of the substituting elements kcal/mole | Difference in constants in % of lowest value | Source |
|---|---|---|---|---|
| GaSb — InSb | Solution over broad concentration interval | 705—644 | 9.4 | (2, 3) |
| AlSb — InSb | | 653—644 | 1.4 | (3) |
| AlSb — GaSb | | 653—705 | 8.0 | Our work |
| GaAs — InAs | | 705—844 | 9.4 | (2) |
| GaP — GaAs | | 1490—1433 | 3.6 | (7) |
| InP — InAs | | 1490—1438 | 3.6 | (7) |
| GaAs — GsSb | No solution over broad concentration interval | 1438—1278 | 12.4 | (2) |
| InAs — InSb | | 1438—1279 | 12.4 | (2) |

The material available at the present time on substitutional solid solutions in systems of the mentioned type is presented in Table 1.

Consideration of the data on Table 1 makes it possible to conclude that the formation of solid solutions of substances of the type $A^{III}B^{V}$ over a broad concentration interval arises when the relative difference in the electrical affinity constants of the substituting elements does not exceed 9.4%.

Undoubtedly, beside this basic factor, the chemical nature of the nonsubstituting element, the purity of the materials used, etc. can also affect the process of substitution.

N. K. Takhtareva and A. S. Borshchevskii took part in the experimental part of the work.

The investigation was carried out in the laboratory of Prof. B. T. Kolomiits, to whom the authors express their sincere appreciation for his constant attention and interest in the work.

## LITERATURE CITED

[1] W. Köster and B. Thoma, Zs. Metallkunde, 46, 293 (1955).

[2] N. A. Goriunova and N. N. Fedorova, J. Tech. Phys. 25, 1339 (1955).

[3] I. E. Gorshkov and N. A. Goriunova, J. Inorg. Chem. No. 4 (1958).

[4] N. A. Goriunova, Bull. Acad. Sci. USSR, Ser. Phys. 21, No. 1, 120 (1957).

[5] B. P. Mitrenin and N. E. Troshin, et al., Problems of the Metallurgy and Physics of Semiconductors (Reports of the 2nd Conference on Semiconductor Materials), Izd. AN SSSR, p. 59.*

[6] H. Welker, Ergebn. exakt. Naturwiss. 29, 275 (1956).

[7] O. G. Folberth, Zs. Naturforsch. 10-a, 6, 502 (1955).

[8] B. V. Nekrasov, Course in General Chemistry, 1953, p. 849.*

[9] N. A. Goriunova, Author's abstract, Doctorate Thesis, Leningrad, 1958.*

Physico-Technical Institute
Academy of Sciences USSR

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* In Russian.

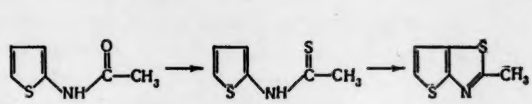
# SYNTHESIS OF 2-METHYL-4,5-THIOPHENO(2',3')THIAZOLE

V. G. Zhiriakov and I. I. Levkoev

(Presented by Academician I. L. Knuniants, February 6, 1958)

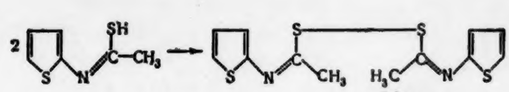
The isosterism of $-CH=CH-$ and $-S-$ groups is well known in thiazole and pyridine derivatives. It seemed of interest to trace the degree of isosterism of these groups through a series of derivatives of benzothiazole and thiophenothiazole, heterocyclic bases containing condensed thiazole and thiophene rings.

In connection with this, it was decided to carry out the synthesis of 2-methyl-4,5-thiopheno(2',3')thiazole. In preparing this compound by a method analogous to the synthesis of 2-methylbenzothiazole [1, 2], it is possible to start from α-amino-β-mercaptothiophene with subsequent reaction with acetic acid or its derivatives or to start with the thioacetyl derivative of α-aminothiophene with further oxidation with potassium ferricyanide. In view of the poor availability of α-amino-β-mercaptothiophene, the second method was selected:



2-Thioacetylaminothiophene was successfully synthesized by the action of phosphorus pentasulfide on 2-acetylaminothiophene [3] by heating in anhydrous benzene.

However, the first attempts to synthesize 2-methyl-4,5-thiopheno(2',3')thiazole by oxidation of 2-thioacetylamidothiophene in a 4-8% solution of sodium hydroxide with potassium ferricyanide ended unsuccessfully. This attempt gave a crystalline substance with a m. p. of 107-108°, which, as was shown, was a disulfide of the structure (I):



(I)

It may be noted that an analogous result was once obtained during an attempt to oxidize α-thioacetamidopyridine under the same conditions [4]. Only later was 2-methyl-4,5-pyrido(2',3')thiazole obtained by this route, apparently under somewhat changed oxidation conditions [5].

Nor did a change in the temperature conditions of the oxidation lead to the desired result. It might be thought that a decrease in the concentration of sodium hydroxide in the reaction mixture would lead to retardation of the oxidation of the hydrogen of the thioacetamido group, and that the difference in the mobility of the hydrogen atom at the β-carbon atom of the thiophene ring and of that of the isothioacetamido group would decrease, which would result in the formation of the desired compound.

Actually, upon the addition of a solution of 2-thioacetamidothiophene in 2% aqueous solution of sodium hydroxide to a dilute solution of potassium ferricyanide, in addition to the disulfide, we were successful in obtaining 2-methyl-4,5-thiopheno(2',3')thiazole in a yield of 10% of theoretical.

The resulting base was a colorless, gradually yellowing oil with a b. p. of 102-104°/7 mm. The compound had the characteristic odor of quinoline bases. It readily forms the picrate, methiodide, and ethiodide.

TABLE 1

| Base | B. p. of base, °C/mm Hg | M. p., °C | | |
|---|---|---|---|---|
| | | picrate | methiodide | ethiodide |
| 2-Methyl-4,5-thiopheno(2',3')thiazole | 118—120/14 | 131—132 | 221—222 | 190—191 |
| 2-Methylbenzothiazole | 118/18 (6) | 153.5 (7) | 218 (8) | 196 (6) |

As seen from Table 1, some of the constants of 2-methyl-4,5-thiopheno(2',3')thiazole and its derivatives are close to those of 2-methylbenzothiazole and its derivatives.

## EXPERIMENTAL

2-Acetylamidothiophene was prepared with a yield of 53% of theoretical by the addition of a solution of sodium hydroxide to a mixture of an aqueous suspension of the double salt of 2-aminothiophene hydrochloride with stannic chloride and acetic anhydride. M. p. 159-160° (161-162° [3]).

The initial 2-aminothiophene double salt was prepared by reduction of 2-nitrothiophene with metallic tin in hydrochloric acid [3], and the 2-nitrothiophene was synthesized by nitration of thiophene with nitric acid, 1.5 sp. gr., in glacial acetic acid [9].

2-Thioacetylamidothiophene. A finely powdered mixture of 20.3 g of 2-acetylamidothiophene and 10.0 g of phosphorus pentasulfide was added, while refluxing, to 250 ml of anhydrous benzene, after which the liquid was refluxed for 2 hours. The benzene layer was decanted, and the tarry residue was refluxed with benzene (3 times with 200 ml). The combined benzene solutions were extracted with a 4% solution of sodium hydroxide (5 times with 230 ml). The resulting aqueous solutions, at 3°, were acidified with 50% acetic acid to a weakly acid reaction to litmus. The precipitate was filtered, carefully washed with water, and dried. The yield was 6.0 g (26.5%). M. p. 98-100°. Crystallization from ethyl alcohol gave slightly yellowish needles with a m. p. of 111-112°.

Found %: N 8.83 $C_6H_7NS_2$. Calculated %: N 8.91.

2-Methyl-4,5-thiopheno(2',3')thiazole. 23.6 g of 2-thioacetylamidothiophene was dissolved at 45° in 700 ml of a 2% aqueous solution of sodium hydroxide. Over a period of 2 hours, the solution, at 0°, was added with vigorous stirring to a solution of 100 g of potassium ferricyanide in 900 ml of water, after which stirring was continued at this same temperature for an additional 2 hours. On the following day, the mixture was carefully extracted with ether (2000 ml). The ether was distilled, and the residue was then steam distilled. The base was extracted from the distillate with 500 ml of ether, the ether extract was dried with potassium carbonate, the ether was distilled, and the residue was distilled under vacuum. The yield was 2.35 g (10.1%). B. p. 102-104°/7 mm (118-120°/14 mm). The product was a colorless oil with a characteristic odor; it yellowed slightly on standing.

Found %: N 8.97 $C_6H_5NS_2$. Calculated %: N 9.02.

On cooling of the filtered liquid remaining in the flask after distillation of the base, the disulfide precipitated; the precipitate was filtered, washed with water, and dried. The weight was 4.9 g. M. p. 103-105°. Crystallization from water gave slightly grayish, long needles with a m. p. of 107-108°. On refluxing with dilute hydrochloric acid, there was vigorous evolution of hydrogen sulfide together with precipitation of sulfur.

Found %: N 8.70. $C_{12}H_{12}N_2S_4$. Calculated %: N 8.97.

Picrate – fine, greenish-yellow prisms (from ethyl alcohol), m. p. 131-132°.

Found %: N 14.36. $C_{12}H_8O_7N_4S_2$. Calculated %: N 14.58.

The methiodide was obtained by heating the base with 1.25 moles of methyl iodide on a boiling water bath for 5 hours; 0.5 mole of methyl iodide was then added, and the heating was continued for another 6 hours. The yield was 75%. The product, slightly greenish, coarse prisms (from anhydrous ethyl alcohol), had a m. p. of 221-222°.

Found %: N 4.63. $C_7H_8NS_2I$. Calculated %: N 4.71.

The ethiodide was prepared by heating the base with 2 moles of ethyl iodide on a boiling water bath for 15 hours, after which 0.5 mole of ethyl iodide was added, and the mixture was heated another 7 hours. The yield was 66%. The product, slightly greenish, coarse prisms (from anhydrous ethyl alcohol), had a m. p. of 190-191°.

Found %: N 4.47. $C_8H_{10}NS_2I$. Calculated %: N 4.50.

The work was carried out at the suggestion of N. N. Sveshnikov, to whom we express our appreciation for his participation in the consideration of the results of the work.

LITERATURE CITED

[1] A. Hofmann, Ber. 13, 1236 (1880).

[2] P. Jacobson, Ber. 19, 1072 (1886).

[3] W. Steinkopf, Lieb. Ann. 403, 17 (1914).

[4] I. L. Knuniants and D. A. Katrenko, J. Gen. Chem. 10, 1167 (1940).

[5] T. Takahashi, T. Jatsuka and J. Onuma, J. Pharm. Soc. Japan, 64, 235 (1944); Chem. Abstr. 45, 4717 (1951).

[6] H. Nitzsche, L. Busch, H. Witzel and H. Gansau, Chem. Ber. 85, 487 (1952).

[7] Y. Mizuno and K. Watanabe, J. Pharm. Soc. Japan, 70, 540 (1950); Chem. Abstr. 45, 7111 (1951).

[8] W. König and W. Meier, J. Prakt. Chem. 109, 324 (1929).

[9] Organic Syntheses, 2, Foreign Lit. Press, 1949, p. 381 (Translation).

All-Union Scientific Research
Kino-Photo Institute

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# ISOTOPE EXCHANGE OF OXYGEN BETWEEN FREE HYDROXYL RADICALS AND WATER

Corresponding Member AN SSSR I. A. Kazarnovskii, N. P. Lipikhin and M. V. Tikhomirov

The free hydroxyl radical plays a great role as an intermediate product in radiation chemistry and in the theory of oxidation processes.

In spite of numerous investigations of the reactivity of this radical, only sparse and contradictory data are available [1-4]. This situation is apparently due to the lack of a method for obtaining the free hydroxyl radical in sufficient concentrations and without atomic hydrogen or heavy metal ions as impurities.

We have investigated the isotope exchange reaction $O^{16}H + H_2O^{18} = H_2O^{16} + O^{18}H$, using potassium ozonide as a new source of free hydroxyl radicals [5, 6].

The decomposition of potassium ozonide by water proceeds instantaneously at room temperature and at 0° with vigorous liberation of oxygen. When water enriched with $H_2O^{18}$ is used, the reaction proceeds according to the equations:

$$KO_3 + H_2\overset{*}{O} = K\overset{*}{O}H + OH + O_2 \tag{1}$$

$$OH + H_2\overset{*}{O} = \overset{*}{O}H + H_2O \tag{2}$$

$$\overset{*}{O}H + \overset{*}{O}H = H_2\overset{*}{O} + \frac{1}{2}\overset{*}{O}_2 \tag{3}$$

$$\overset{*}{O}H + \overset{*}{O}H = H_2\overset{*}{O}_2 \tag{4}$$

As investigations in our laboratory have shown, the rate of the disproportionation of hydroxyls is 4-5 times higher than the rate of their dimerization.

If the rate of isotope exchange of oxygen between free hydroxyls and water [Equation (2)] is not insignificantly small in comparison to the rates of the disproportionation and dimerization of hydroxyl radicals, the gaseous oxygen liberated during the decomposition of potassium ozonide by water will be enriched with the isotope $O^{18}$. Our experiments confirmed this.

The potassium ozonide used had the following composition: $KO_3$, 89.3%; KOH, 8.4%; $HO_2$ (in the form of $KOH \cdot H_2O$) 2.3%.

The decomposition of weighed portions of potassium ozonide by water containing 1.38% $H_2O^{18}$ was carried out in the apparatus shown in Fig. 1A.

The reaction vessel 1, with a volume of 35 cc, was fitted with a magnetic stirrer 2, which rotated at a rate of 500 rpm. The thin-walled glass capillary 4, 2.2 mm in diameter and with a small glass rod sealed to one end, was first filled with potassium ozonide powder in a dry cabinet, weighed, and sealed.

Prior to an experiment, the capillary containing the sample was sealed to a glass tube containing a lead weight, 6, and suspended by a fine silk thread from the ground glass plug 8. The initial solution was introduced into vessel 1, and the apparatus was then joined by means of ground glass joint 9 to the part of the apparatus

(Fig. 1B) consisting of gas buret 11 and tube 12 for collection of the oxygen sample. The apparatus permitted the decomposition of potassium ozonide to be carried out in an atmosphere of nitrogen or under vacuum.

On rotation of the ground glass plug 8 (Fig. 1), the weight and the capillary containing powdered $KO_3$ descended, and the capillary, on reaching the roughened surface of the rotating quartz-jacketed stirrer, was gradually disintegrated. The introduction of the potassium ozonide powder was usually carried out over a period of 3-5 minutes.

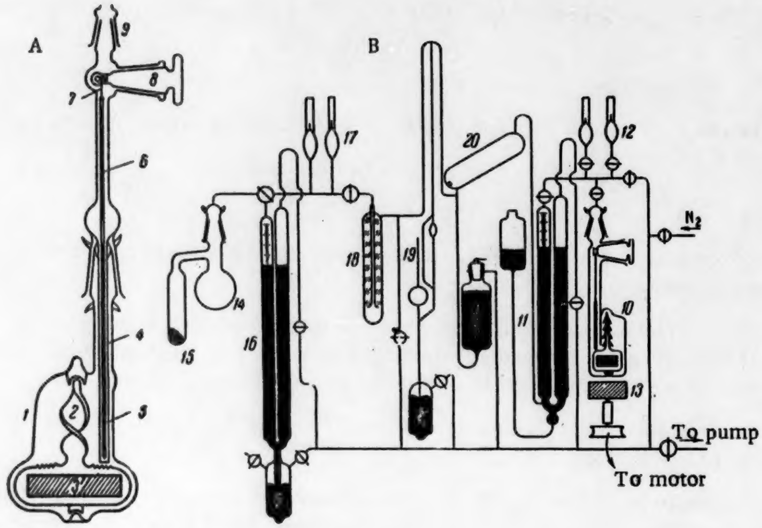


Fig. 1. Diagram of the experimental apparatus. A) Apparatus for the decomposition of potassium ozonide with water: 1) Reaction vessel, 2) quartz stirrer, 3) magnet, 4) capillary containing a weighed amount of $KO_3$, 5) sleeve, 6) lead weight, 7) silk thread, 8) ground glass plug for lowering capillary, 9) ground glass joint. B) apparatus for the investigation of the isotopic composition of oxygen from the decomposition of $KO_3$ by water: 10) apparatus for the decomposition of potassium ozonide by water; 11 and 16) gas burets, 12 and 17) tubes for collection of oxygen sample, 13) rotating magnet, 14 and 15) apparatus for degasification and decomposition of hydrogen peroxide, 18) trap, 19) McLeod gauge, 20) Toepler pump.

The evolved oxygen (mixed with nitrogen) was collected in gas buret 11 and then transferred to evacuated glass sample tube 12 for mass spectrographic analysis. The analysis was carried out in a Nier-type mass spectrometer, which has previously been described in detail [6]. The error in the determinations of $O^{18}$ did not exceed ± 2% of the measured values. Cylinder oxygen, which contained 0.204% $O^{18}$, was used as a standard. The degree of exchange was related to the total amount of hydroxyl radicals after deduction of the amount consumed by the formation of hydrogen peroxide (which was determined with an 0.1 N solution of $KMnO_4$. In the experiments on the formation of $H_2O_2$, not more than 15% of the hydroxyl radicals was so consumed.

Table 1 presents the results of the determination of the isotopic composition of the oxygen evolved during the decomposition of potassium ozonide by heavy water and also the degree of exchange found. As seen from these data, the degree of exchange of free hydroxyl radical with water at +20 and 0° is about 10%, and does not depend on the pH of the solution. This independence of the pH of the solution confirms that the exchange actually proceeds between free hydroxyl and water, and not between hydroxyl and hydroxyl ions.

In interpreting the relatively low degree of exchange, it is necessary to take into account that this reaction is concurrent with the very fast reactions of the disproportionation and dimerization of the free hydroxyl radicals.

TABLE 1

Isotope Exchange of Free Hydroxyl with Water Containing 1.38% $H_2O^{18}$

| Weight of potassium ozonide, mg | Initial solution | pH of final solution | Amount of OH formed, mmoles. | Amount of oxygen evolved, cc (0°, 760 mm) | Content of $O^{18}$ in evolved oxygen, atom % | Degree of isotope exchange, % |
|---|---|---|---|---|---|---|
| | | | At a temperature of 20° | | | |
| 217.3 | 10 cc $H_2O^*$ | 13.4 | 2.23 | 62.4 | 0.226 | 8.9 |
| 191.3 | 10 cc $H_2O^*$ | 13.3 | 1.96 | 56.3 | 0.226 | 9.5 |
| 157.0 | 35 cc $H_2O^*$ | 12.7 | 1.61 | 44.3 | 0.229 | 11.0 |
| 161.8 | 10 cc $H_2O^*$+ +0.17 g $H_2SO_4$ [1] | 0.8 | 1.66 | 48.0 | 0.227 | 9.8 |
| 163.5 | 35 cc $H_2O^*$+ +0.60 g $H_2SO_4$ | 0.5 | 1.67 | 46.1 | 0.226 | 10.3 |
| | | | | Average | | 9.9±1 |
| 134.6 | 35 cc $H_2O$ | 12.7 | 1.54 | 41.9 | 0.204 [2] | |
| | | | At a temperature of 0° | | | |
| 179.6 | 35 cc $H_2O^*$ | 12.8 | 1.84 | 50.0 | 0.229 | 10.5 |
| 155.0 | 35 cc $H_2O^*$ | 12.7 | 1.59 | 43.5 | 0.227 | 9.8 |
| 171.1 | 35 cc $H_2O^*$+ +0.60 g $H_2SO_4$ | 0.5 | 1.75 | 47.6 | 0.231 | 12.8 |
| 165.1 | 35 cc $H_2O^*$+ +0.60 g $H_2SO_4$ | 0.5 | 1.69 | 45.3 | 0.226 | 10.6 |
| | | | | Average | | 10.9±1 |

*Here and further on, 0.35 N $H_2SO_4$.

**This control experiment showed that during the decomposition of potassium ozonide with doubly distilled water, the oxygen evolved had the normal isotopic composition.

It also seemed of interest to determine the isotopic composition of the oxygen in the hydrogen peroxide formed. It would be expected that the enrichment of the hydrogen peroxide with $O^{18}$ oxygen isotope would be several times greater than in the oxygen evolved directly during the decomposition of $KO_3$ by heavy water, since the molecular oxygen, which comprises more than $^4/_5$ of the total oxygen [Equation (1)], does not exchange with water.

Our experiments completely confirmed this prediction. The small amount of hydrogen peroxide formed under the conditions of our experiments was troublesome. In these experiments, the decomposition of $KO_3$ with water containing 1.57-3.00% $H_2O^{18}$ was carried out in an apparatus with a magnetic stirrer; the apparatus was similar to that described above, but had a volume of 10 cc.

After decomposition of the potassium ozonide with water, the resulting hydrogen peroxide was determined on part of the solution by titration with an 0.1 N solution of $KMnO_4$. The other part of the reaction solution (7 cc) was transferred to the small flask 14, and 3 cc of an acidified 0.16 N solution of cerium sulfate was placed in tube 15. Preliminary degasification of the solutions was carried out by alternate freezing and thawing under vacuum (0.01 mm Hg). The system was then pumped to a vacuum of $1\text{-}3 \cdot 10^{-3}$ mm Hg by means of Toepler pump 20, and the hydrogen peroxide was then distilled at room temperature from the solution to tube 15, which was immersed in a Dewar of solid carbon dioxide.

At the conclusion of the distillation, the system was again evacuated to $10^{-3}$ mm Hg, the contents of tube 15 were thawed out, and the hydrogen peroxide was decomposed by the cerium sulfate; the reaction proceeded according to the equation:

$$2Ce^{4+} + H_2O_2^{\bullet} = 2Ce^{3+} + 2H^+ + O_2^{\bullet}. \qquad (5)^*$$

*It has been established that during this reaction, the oxygen is liberated quantitatively from the hydrogen peroxide, and its composition does not depend on the isotope composition of the water [4, 7, 8].

The oxygen evolved was transferred to tube 17 for mass spectrographic analysis.

The data on the isotopic composition of the oxygen from the hydrogen peroxide are presented in Table 2. It follows from these data that in the oxygen from the hydrogen peroxide, enrichment with $O^{18}$ isotope was 2.2-4.7 times (or 3 times on the average) greater than in the oxygen evolved directly during the decomposition of potassium ozonide by water.

TABLE 2

Isotopic Composition of Oyxgen in Hydrogen Peroxide Formed During the Decomposition of Potassium Ozonide at 0° by Water Enriched with $H_2O^{18}$ and 0°*

| Expt. No. | Weight of $KO_3$, mg | Initial solution ($H_2O^*$) | pH of final solution | Amount of OH formed, mmoles | Amt. of oxygen evolved during decompn. of $KO_3$ by water, cc (0°, 760 mm) | Content of $O^{18}$ in evolved oxygen, atom % | Amt. of oxygen evolved during decompn. of $H_2O_2$, cc (0°, 760 mm) | Extent of consumption of hydroxyl in the formation of $H_2O_2$, % | Content of $O^{18}$ in $H_2O_2$ oxygen, atom, % |
|---|---|---|---|---|---|---|---|---|---|
| 32 | 257.1 | 6cc 0,99 *N* $H_2SO_4$ | 0.3 | 2,60 | 70.8 | 0.221 | 1.14 | 3.9 | 0.273 |
| 34 | 199.2 | 8 cc 0,38 *N* $H_2SO_4$ | 1.0 | 1.81 | 50.2 | 0.225 | 1.51 | 7.4 | 0.250 |
| 35 | 159.6 | 8 cc 0,38 *N* $H_2SO_4$ | 0.8 | 1.48 | 39.8 | 0.221 | 1.28 | 7.7 | 0.248 |
| 50 | 233.1 | 10 cc 0,58 *N* $H_2SO_4$ | 0.5 | 2.33 | 64.3 | 0.227 | 1.15 | 9.8 | 0.262 |
| 51 | 256.9 | Same | 0.5 | 2.57 | 71.4 | 0.222 | 1.35 | 10.4 | 0.252 |
| 52 | 283.9 | " | 0.6 | 2.89 | 78.2 | 0.216 | 1.81 | 12.8 | 0.249 |
| 56 | 253.1 | " | 0.6 | 2.53 | 69.9 | 0.216 | 1.49 | 11.8 | 0.259 |
| 57 | 252.7 | 10 cc 0.54 *N* $H_2SO_4$ | 0.6 | 2.52 | 68.7 | 0.224 | 1.23 | 11.8 | 0.246 |

*In Experiment No. 32, the water used contained 1.57% $H_2O^{18}$; in Experiments No. 34, 35, 56, and 57 – 2.78% $H_2O^{18}$; in Experiments Nos. 51 and 52 – 3.00% $H_2O^{18}$.

The deviation of the found degree of enrichment from the calculated value (calculation requires 5-5.5 times, not 3 times) can be attributed to errors due to the very small amounts of oxygen (1-2 cc) liberated from the hydrogen peroxide under the conditions of our experiments, to the difficulty of complete gasification of the $H_2O_2$ solutions, etc.

These results confirm that during the decomposition of potassium ozonide with water, the hydrogen peroxide is actually formed from the free hydroxyl radicals.

Considering the question of the nature of the diffusion of free hydroxyl during radiolysis of water, Dainton [3], on the basis of unpublished experiments showing the absence of rapid exchange between free hydroxyl radicals and water, was led to the conclusion that this radical diffuses by a normal mechanism, and not by a Grotthus mechanism.

Our experiments, which disclosed the presence of a very rapid exchange, lead to the contrary conclusion and indicate the presence of an interaction between free hydroxyl radicals and water in the sense of the Grotthus views.

This result is essential for understanding the reactivity of the free hydroxyl radical.

## LITERATURE CITED


[1] O. L. Forchheimer and H. Taube, J. Am. Chem. Soc. 74, 3705 (1952).

[2] O. L. Forchheimer and H. Taube, J. Am. Chem. Soc. 76, 2090 (1954).

[3] F. S. Dainton, Ann. Rep. Progr. Chem. 45, 27 (1948).

[4] E. S. Hart, S. Gordon and D. Hutchison, J. Am. Chem. Soc. 75, 6165 (1953).

[5] I. A. Kazarnovskii, G. P. Nikol'skii and T. A. Abletsova, Proc. Acad. Sci. USSR, 64, 69 (1949); P. Whaley and J. Kleinberg, J. Am. Chem. Soc. 73, 79 (1951).

[6] I. A. Kazarnovskii, Z. A. Bardasar'ian and N. P. Lipikhin, "A New Source of the Free Hydroxyl Radical in Solution,"* Report to the All-Union Conference on Chemical Kinetics, July 23, 1955 (in press).*

[7] B. V. Ottesen, L. M. Gol'din, M. I. Men'shikov and T. M. Kukavadze, Problems of Med. Chem. 2, 79 (1950).

[8] A. E. Cahill and H. Taube, J. Am. Chem. Soc. 74, 2312 (1952).

[9] M. Dole, DeForest, P. Rudd, Cordon, R. Muchow and E. Comte, J. Chem. Phys. 20, 961 (1952).

L. Ia. Karpov Physicochemical
Scientific Research Institute

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* In Russian.

# X-RAY INVESTIGATION OF THE URANATES OF THE ALKALI ELEMENTS

L. M. Kovba, E. A. Ippolitova, Iu. P. Simanov and Corresponding Member AN SSSR Vikt. I. Spitsyn

Information is available in the literature on the structures of the monouranates of magnesium [1], calcium [2], strontium [2], barium [3], and $\beta UO_2(OH)_2$ [4]. In the structures of the monouranates of magnesium, barium, and $\beta$-$UO_2(OH)_2$, the somewhat distorted $UO_6$ octahedra form either pseudotetragonal layers (barium uranate, $\beta$-$UO_2(OH)_2$) or chains (magnesium uranate) having the composition $(UO_2)O_2$. Hexagonal layers of the composition $(UO_2)O_2$ occur in the calcium and strontium uranate structures. In this case, the uranium atoms are surrounded by oxygen atoms at the corners of a somewhat distorted cube. Hexagonal or pseudohexagonal layers, analogous to those in calcium uranate, have also been found in the structures of lithium, sodium, and potassium uranates [5]; however, more detailed information on the structures of the alkali metal uranates has not been published. There are no experimental data available on the structures of the diuranates.

We prepared single crystals of the normal uranates of lithium ($\alpha$-modification) and sodium ($\beta$-modification) and of the diuranates of sodium, potassium, and rubidium. These compounds were studied by the Laue, oscillation and powder methods. We were unable to prepare single crystals of $\alpha$-$Na_2UO_4$, $K_2UO_4$, $Rb_2UO_4$, and $Cs_2UO_4$, and these compounds were studied by the powder method. In all cases, the intensity of the reflections was determined visually by the ten-point method from debyegrams. All data are reported in angstroms.

TABLE 1

Some X-Ray Data for Mono- and Diuranates of the Alkali Elements

| Compound | Space group | $a$ | $b$ | $c$ | $Z$ | $\rho_{x\text{-ray}}$ | $\rho_{pycn}$ |
|---|---|---|---|---|---|---|---|
| $\alpha$-$Li_2UO_4$ | *Fmmm* | 6.06 | 5.13 | 10.52 | 4 | 6.43 | 6.13* |
| $\alpha$-$Na_2UO_4$ | *Cmmm* | 9.74 | 5.72 | 3.49 | 2 | 5.94 | — |
| $\beta$-$Na_2UO_4$ | *Fmmm* | 5.97 | 5.795 | 11.68 | 4 | 5.73 | 5.51* |
| $K_2UO_4$ | *I 4/mmm* | 4.335 | — | 13.10 | 2 | 5.15 | 4.66* |
| $Rb_2UO_4$ | *I 4/mmm* | 4.345 | — | 13.83 | 2 | 6.02 | 5.42 |
| $Cs_2UO_4$ | *I 4/mmm* | 4.38 | — | 14.79 | 2 | 6.65 | 6.04 |
| $Na_2U_2O_7$ | $R\bar{3}m$ | 3.93 | — | 17.76 | 1/2** | 6.17 | — |
| $K_2U_2O_7$ | $R\bar{3}m$ | 3.98 | — | 19.67 | 1/2** | 6.15 | 6.12 |
| $Rb_2U_2O_7$ | $R\bar{3}m$ | 4.00 | — | 20.77 | 1/2** | 6.57 | — |

*Reference [7] reports the following data for $Li_2UO_4$, $Na_2UO_4$, and $K_2UO_4$ (respectively): 6.61, 5.06, and 4.98. The last two figures are too low and the first is apparently too high.

**For a rhombohedral cell.

Table 1 presents the values of the lattice parameters for the uranates studied, their space groups and their densities, both calculated from x-ray data and determined pycnometrically.

The structures were determined by trial and geometric and crystallochemical arguments. The estimated intensities confirm the structures described below.

Tetragonal and pseudotetragonal layers of $(UO_2)O_2$ similar to those in the $BaUO_4$ and $\beta$-$UO_2(OH)_2$ structures [3, 4] were found in the structures of $\alpha$-$Li_2UO_4$, $\beta$-$Na_2UO_4$, $K_2UO_4$, $Rb_2UO_4$, and $Cs_2UO_4$. The atoms of the alkali elements were disposed between the layers.

The normal uranates of potassium, rubidium, and cesium have the same structure as $K_2NiF_4$ [6]: 2U in (a); $4\overset{I}{Me}$ in (e); $4O_I$ in (c) (here and throughout the paper, $O_I$ is oxygen in the uranyl group). The values of the parameters $Z_{\overset{I}{Me}}$ ($\overset{I}{Me}$ represents an alkali element) and $Z_{O_I}$ the values of the interatomic distances U−O and $\overset{I}{Me}$−O, and the shortest distance O−O are presented in Table 2.

TABLE 2

Certain Information on the Structures of $\alpha$-$Li_2UO_4$, $\beta$-$NaU_2O_4$, $K_2UO_4$, $Rb_2UO_4$, and $Cs_2UO_4$

| Compound | $z_{O_I}$ | $z_{\overset{I}{Me}}$ | $U-2O_I$ | $U-4O_{II}$ | $\overset{I}{Me}-O_I$ | $\overset{I}{Me}-4O_{II}$ | $\overset{I}{Me}-4O_I$ | O−O* |
|---|---|---|---|---|---|---|---|---|
| $\alpha$-$Li_2UO_4$ | 0.18 | 0.39[2] | 1.89 | 1.98 | 2.14 | 2.32 | 2.65—3.1 | 2.56 |
| | 0.18 | —[3] | 1.89 | 1.98 | — | 2.63[4] | 2.12 | 2.56 |
| $\beta$-$Na_2UO_4$ | 0.165 | 0.38 | 1.93 | 2.12 | 2.52 | 2.52 | 2.96—3.04 | 2.88 |
| $K_2UO_4$ | 0.145 | 0.36 | 1.90 | 2.17 | 2.82 | 2.84 | 3.07 | 2.86 |
| $Rb_2UO_4$ | 0.138 | 0.354 | 1.91 | 2.17 | 2.99 | 2.97 | 3.07 | 2.87 |
| $Cs_2UO_4$ | 0.129 | 0.344 | 1.91 | 2.19 | 3.18 | 3.18 | 3.16 | 2.89 |

* Shortest distance. [2] Li in 8 (i). [3] Li in 8 (f). [4] $Li-2O_{II}$.

The structure of $\beta$-$Na_2UO_4$ is a distorted rhombohedral structure of the type of $K_2NiF_4$: 4U in (a); 8Na in (i); $8O_I$ in (i); $8O_{II}$ in (e). The values of the parameters $Z_{Na}$ and $ZO_I$ and the interatomic distances are presented in Table 2. A somewhat different disposition of the atoms of the alkali element than in $\beta$-$Na_2UO_4$ is possible in lithium uranate, namely, 8Li in (f). The disposition of the remaining atoms is the same in $\beta$-$Na_2UO_4$ and $\alpha$-$Li_2UO_4$. Data for both variants in the distribution of lithium atoms are presented in Table 2.

The structure of $\alpha$-$NaU_2O_4$ contains infinite chains of $UO_6$ octahedra joined at their common edges. 2U in (a); 4Na in (f); $4O_I$ in (i) with y = 0.195; $4O_{II}$ in (h) with x = 0.245; $U-2O_I = 1.90$; $U-4O_{II} = 2.24$; $Na-2O_{II} = 2.44$; $Na-4O_I = 2.32$; shortest O−O distance is 2.73.

The structures described above for lithium, sodium, and potassium monouranates differ from the structures of these compounds as studied by Zachariasen [5].

The structures of sodium, potassium, and rubidium diuranates are defect structures of the type of $CaUO_4$: U in (a); $\overset{I}{Me}$ in (b); $2O_I$ and $1\frac{1}{2}O_{II}$ in (c). The parameters $X_{O_I}$ and $X_{O_{II}}$, together with the interatomic distances, are presented in Table 3. A hexagonal layer of the composition $UO_{3,5}$ was detected in these structures.

TABLE 3

Certain Information on the Structures of Sodium, Potassium, and Rubidium Diuranates

| Compound | $x_{O_I}$ | $x_{O_{II}}$ | $U-2O_I$ | $U-6O_{II}$ | $\overset{I}{Me}-6O_I$ | $\overset{I}{Me}-2O_{II}$ |
|---|---|---|---|---|---|---|
| $Na_2U_2O_7$ | 0.108 | 0.357 | 1.92 | 2.35 | 2.50 | 2.54 |
| $K_2U_2O_7$ | 0.098 | 0.357 | 1.93 | 2.38 | 2.67 | 2.81 |
| $Rb_2U_2O_7$ | 0.093 | 0.355 | 1.93 | 2.39 | 2.78 | 3.01 |

The oxygen atoms can be partially replaced by fluorine with the formation of the fluorouranate, for example, $NaUO_3F$, which also has the same structure as $CaUO_4$. On calcination in air, $NaUO_3F$ is gradually converted to sodium diuranate. The material remains single phase throughout the conversion, so that a continuous region of solid solutions probably exists between the sodium fluorouranate and diuranate.

By reduction of sodium and potassium diuranates at 450-500°, we obtained sodium and potassium uranates (V) having the composition $MeUO_3$, which were studied by the powder method. Both compounds have a structure of the perovskite type. For $NaUO_3$: $a\sin\beta = b = c\sin\beta = 4.129 \pm 0.002$; $\beta = 88° 36' \pm 6'$; $\rho_{x\text{-ray}} = 7.38$; for $KUO_3$: $a = 4.290 \pm 0.001$; $\rho_{x\text{-ray}} = 6.85$. It was shown with $KUO_3$ that uranates (V) have a narrow region of homogeneity (the lattice constants do not change either with an excess of potassium present (by reduction of $K_2UO_4$) or with a deficiency of potassium – along with $KUO_3$, the latter samples always contained uranium dioxide). Uranates (V) are readily soluble in nitric acid and dissolve slowly in acetic acid. Thus, the uranates (V) are not analogs of the "tungsten bronzes." In agreement with the data of Rüdorff and Leutner [7], uranates (V) are not formed by reduction of $Li_2UO_4$ and $Na_2UO_4$. $Rb_2UO_3$, with the parameter of a cubic pseudo cell d = 4.316, is formed by reduction of $Rb_2UO_4$. Reduction of $Cs_2UO_4$ does not give uranates (V) or (IV).

## LITERATURE CITED


[1] W. H. Zachariasen, Acta Cryst. 7, 783 (1954).

[2] W. H. Zachariasen, Acta Cryst. 1, 281 (1948).

[3] S. Samson and L. G. Sillen, Ark. Kemi. Min., Geol. 25A, 21, 16 (1947).

[4] G. Bergström and G. Lundgren, Acta Chem. Scand. 10, 673 (1956).

[5] W. H. Zachariasen, Manh. Prakt. Rep., CP – 2611, 14 (cited in Acta Cryst. 7, 795 (1954)).

[6] D. Balz and K. Plieth, Zs. Elektrochem. 59, 545 (1955).

[7] W. Rüdorff and H. Leutner, Zs. anorg. Chem. 292, 193 (1957).



M. V. Lomonosov Moscow
State University



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# THE INTRODUCTION OF DIHYROXYCARBOXYLIC, GLYCERIN, AND HYDROXYACETONE SIDE CHAINS INTO ORTHOMETHYLCYCLOHEXANONE AND THE STEREOCHEMISTRY OF THE RESULTING COMPOUNDS

Academician I. N. Nazarov and A. A. Akhrem

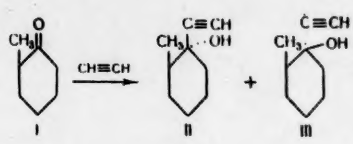
We recently described several methods of introducing oxidized side chains into cyclic compounds, these methods being based on available acetylenic alcohols and their derivatives [1]. As is well known, the introduction of a dihydroxyacetone side chain is an important point in the problem of the partial and total synthesis of cortical steroids in general and of cortisone and its analogs in particular.

Studying the addition of hypobromous acid to tertiary acetylenic alcohols and their acetates, we were the first [1] to observe that, in the case of tert-acetylenic alcohols, this reaction proceeds anomalously and leads to the formation of unsaturated dibromides in place of the expected dibromoketols.

In the present communication, we briefly report the results of our investigations of the introduction of an oxidized side chain into orthomethylcyclohexanone (I).

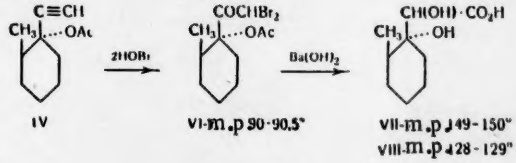
The condensation of ketone I with acetylene under pressure [2] in the presence of powdered potassium hydroxide gives, in high yield, 2-methyl-1-ethynylcyclohexanol in the form of two epimers: a crystalline material (II) with a m.p. of 56-57° and a liquid (III) with a b. p. of 75°/15 mm and $n_D^{20}$ 1.4770. The ratio of the epimers was 3 : 2, and it apparently depends on the conditions of the synthesis [3].

We have previously shown [4] that the crystalline acetylenic alcohol (II) has a cis-configuration, while the liquid (III) is the trans-isomer.

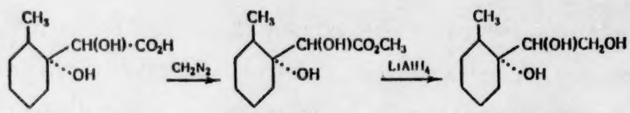


Acetylation of alcohols II and III with an excess of acetic anhydride gives the acetates IV and V, respectively.

The normal addition reaction across the triple bond takes place during the action of hypobromous acid on cis-acetate IV, and the crystalline acetate cis-1-(ω-dibromoacetyl)-2-methylcyclohexanol (VI) is formed in 95% yield.



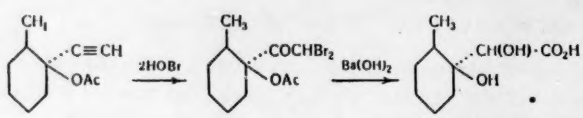
With the action of an aqueous solution of barium hydroxide on the acetate of the cis-dibromoketol (VI), an intramolecular rearrangement, previously described by us [1], took place, and a mixture of two isomeric dihydroxycarboxylic acids (VII and VIII) was formed in 50% yield; these acids differed in the configuration of the secondary hydroxyl. Acid VII predominates in the mixture. Acids VII and VIII, when reacted with an ethereal solution of diazomethane, give the methyl esters IX and X, which are reduced by lithium aluminum hydride to the triols XI and XII.




VII-m.p.149-150°  IX-liquid  XI-m.p.88-88.5°
VIII-m.p.128-129°  X-m.p.73-74°  XII-m.p.90-90,5°

A mixture of the isomeric alcohols XI and XII melted at 50-55°.

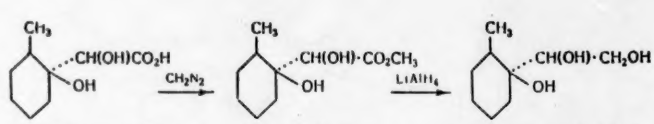
Similar conversions were also carried out with trans-acetate V.




V  XIII  XIV-m.p.156-156,5°
XV-m.p.109-110°

The trans-dibromketol XIII was prepared under the above-described conditions, and the action of barium hydroxide on this compound gave a 50% yield of a mixture of two isomeric trans-dihydroxy acids (XIV and XV) with melting points of 156-156.5° and 109-110°, respectively.

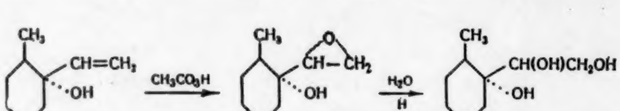
The trans-acids XIV and XV were converted to their methyl esters XVI and XVII, and reduction of the esters with lithium aluminum hydride gave the triols XVIII and XIX:




XIV-m.p.156-156.5°  XVI-m.p.91-91.5°  XVIII-m.p.125-125,5°
XV-m.p.109-110°  XVII-m.p.53-54°  XIX-m.p.88-88.5°

The individual triols XI and XIX had melting points of 88-88.5°, but a mixed sample melted with a sharp depression of the melting point to 55-65°.

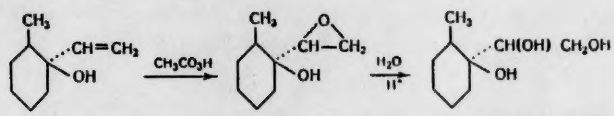
Selective catalytic hydrogenation of cis-acetylenic alcohol II over Pd catalyst gave a high yield of cis-2-methyl-1-vinylcyclohexanol (XX), oxidation of which by the Prilezhaev method with peracetic acid in chloroform gave an 80% yield of a mixture of the isomeric glycidyl alcohols XXI and XXII, the latter a liquid and the former melting at 43-43.5°. Glycidyl alcohol XXII was produced in the greater amount.




XX  XXI-m.p.43-43.5°  XI-m.p.88-88.5°
XXII-liquid  XII-m.p.89-90°

When heated with dilute acid, glycide XXI, with a m. p. of 43-43.5°, was smoothly converted to the above-described triol (XI) with a m. p. of 88-88.5°. Hydrolysis of glycide XXII gave a small amount of the above-described triol XII with a m. p. of 89-90°. That these substances were identical was shown by a mixed m. p.

Oxidation of trans-2-methyl-1-vinylcyclohexanol (XXIII) with peracetic acid in chloroform gave two crystalline glycidyl alcohols (XXIV and XXV), which were epimeric with respect to the asymmetric carbon atom of the oxidized side chain. Glycide XXIV was produced in the greater amount.



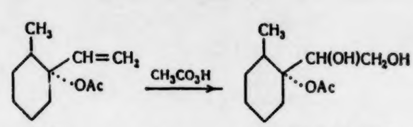
XXIII — XXIV m.p. 73-74°, XXV-m.p. 40-41° — XVIII-m.p. 125-125.5°, XIX-m.p. 88-88.5°

Hydrolysis of glycide XXIV with dilute acid gave a good yield of the above-described triol XVIII with a m. p. of 125-125.5°, which was also prepared by reduction of the ester of the trans-dihydroxy acid by means of lithium aluminum hydride. The action of dilute acid hydrolyzed glycide XXV with the formation of triol XIX with m. p. 88-88.5°; this compound was not obtained on reduction of the ester of dihydroxy acid XVII. It follows from the experimental results that oxidation of the unsaturated alcohols XX and XXIII with peracetic acid is not strictly selective and leads to the formation of all isomers of glycidyl alcohols (XXI, XXII, XXIV, and XXV) predicted by theory. A mixture of glycide XXI, with a m. p. of 43-43.5°, and glycide XXV, with a m. p. of 40-41°, melted at room temperature.

Selective catalytic hydrogenation over Pd catalyst of cis-acetate IV and trans-acetate V gave the acetates of cis-2-methyl-1-vinylcylohexanol (XXVII) and trans-2-methyl-1-vinylcyclohexanol, respectively.

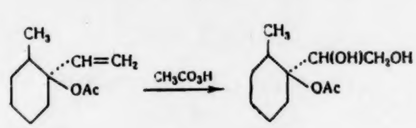
Oxidation of cis-acetate XXVII with peracetic acid gave a mixture of two epimeric monoacetates of the triols XXIX and XXX with melting points of 99-100° and 57-58°, respectively.

Normal products of the oxidation reaction — acetates of glycidyl alcohol XXXI — were not isolated.



XXVII — XXIX-m.p. 99-100°, XXX-m.p. 57-58° — XXXI

That the acetates XXIX and XXX contain one acetyl group was shown by hydrolysis. The above-described triol XI, with a m. p. of 88°, was isolated from the products of the hydrolysis of acetate XXIX, which has an m. p. of 99-100°. Saponification of acetate XXX, which has a m. p. of 57-58°, gave the above-described triol XII with a m. p. of 90-90.5°. A similar result was obtained by oxidation of trans-acetate XXVIII.

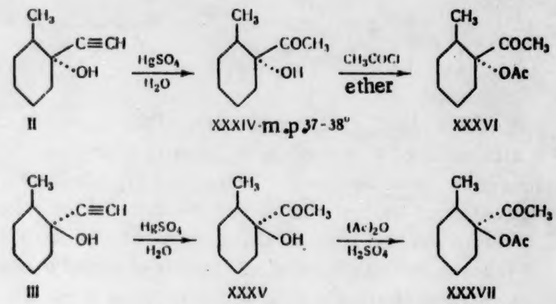


XXVIII — XXXIII — XXXII

In this case, instead of the expected acetate of glycidyl alcohol XXXII, a mixture of the monoacetates of the isomeric triols XXXIII was isolated, hydrolysis of which gave two triols (XIX and XXVI) with melting points of 86-87° and 111-112°, respectively. Triol XXVI was isolated in the greater amount.

These results indicate that oxidation of acetates of tertiary vinyl alcohols with peracetic acid, in contrast to the oxidation of the corresponding vinyl alcohols and acetates of allyl alcohols, does not lead to the formation of the normal oxidation products — acetates of glycidyl alcohols [1].

As is well known, conformation analysis permits connecting the stereochemisty of a molecule with its reactivity. It therefore seemed of interest to use the epimeric acetylenic alcohols II and III to study the hydration of the triple bond and also the acetylation of the tertiary hydroxyl with the aim of establishing the dependence of the reaction rates on the equatorial or axial location of the substituent. Hydration of the cis-alcohol II in methanol solution in the presence of mercuric sulfate and sulfuric acid gave an almost quantitative yield of the cis-α-ketol XXXIV with a m. p. of 37-38° [6]. The trans-alcohol III hydrated to the liquid trans-α-ketol XXXV at a somewhat higher rate but with a lower yield.




A sharper distinction was observed during the acetylation of the hydroxyl group of the epimeric pair of α-ketols XXXIV and XXXV. The cis-α-ketol XXXIV acetylated under milder conditions, by refluxing with an excess of acetyl chloride in ether. The trans-α-ketol XXXV acetylated only under the action of acetic anhydride and in the presence of concentrated sulfuric acid. This gave the acetates XXXVI and XXXVII in almost quantitative yields. This result indicates that in the cis-α-ketol XXXIV the tertiary hydroxyl apparently has an equatorial configuration, while in the trans-α-ketol XXXV it has an axial position [7]. This conclusion agrees with data recently obtained during a study of the Raman spectra [8].

## LITERATURE CITED


[1] I. N. Nazarov and A. A. Akhrem, J. Gen. Chem. 26, 1186 (1956).*

[2] I. N. Nazarov and V. F. Riabchenko, J. Gen. Chem. 23, 1900 (1953).*

[3] J. D. Billimoria, J. Chem. Soc. 1953, 2626.

[4] I. N. Nazarov, A. V. Kamernitskii and A. A. Akhrem, J. Gen. Chem. 28, No. 6 (1958).*

[5] H. Orloff, Chem. Rev. 54, 347 (1954); D. Barton and R. Cookson, Quart. Rev. 10, 44 (1956); I. N. Nazarov and L. D. Bergel'son, Proc. Chem. 26, 3 (1957).

[6] I. N. Nazarov and A. A. Akhrem, J. Gen. Chem. 28, No. 7 (1958).*

[7] I. Pasqual, J. Sistare and A. Regas, J. Chem. Soc. 1939, 1943.

[8] M. I. Batuev, A. A. Akhrem, A. D. Matveeva and I. N. Nazarov, Proc. Acad. Sci. USSR, 117, No. 3 (1957).*



N. D. Zelinskii Institute of
Organic Chemistry
Academy of Sciences USSR



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# PREPARATION OF METALLIC DERIVATIVES OF VINYL ALCOHOL

Academician A. N. Nesmeianov, I. F. Lutsenko and R. M. Khomutov

The most interesting feature of $\alpha$-monomercurized carbonyl compounds is their tendency toward dual reaction (at the C and at the O) and the formation of two series of derivatives. In the first case, reaction products are formed corresponding to the direct substitution of the mercury atom, while in the second case, the reaction proceeds with transfer of the reactive center of the molecule owing to the clearly expressed conjugation of the Hg–C and C–O-bonds ($\sigma-\pi$-conjugation) [1-4].

In the present article, we report on our studies of a new group of reactions of monomercurized carbonyl compounds which also proceed with transfer of the reactive center. The reactions described below permit easy accomplishment of the transfer from C–metal carbonyl derivatives to the O–metal derivatives, and, particularly, to obtain in high yield metallic derivatives of the simplest enol–vinyl alcohol.

These results were partially reported by us in 1955 in Zurich at the 14th International Congress on Theoretical and Applied Chemistry.

Experiments were carried out on the preparation of lithium and sodium vinylates by cleavage of monomercurized acetaldehyde with metallic lithium and sodium in benzene and toluene. These attempts were unsuccessful, since even with many hours of refluxing no cleavage of the Hg–C bond was observed.

We were able to obtain lithium and sodium vinylates as individual compounds by cleaving the Hg–C bond of mercury derivatives of aldehydes and ketones with solutions of the alkali metals in liquid ammonia.

$$Hg(CH_2CHO)_2 + Li/NH_3 \rightarrow Li/Hg + 2CH_2 = CHOLi.$$

These compounds are colorless crystalline substances. Lithium vinylate is soluble in ether and benzene; sodium vinylate is soluble neither in ether nor in benzene.

The structure and composition of these compounds was proved by analysis, by titration of weighed portions with acid, and by hydrolysis to acetaldehyde. The i.r. spectrum of lithium vinylate also confirmed the data on the structure of this compound. The band characteristic of the carbonyl group was absent from the i. r. spectrum, and there was a band at 1600 $cm^{-1}$ which is characteristic of a double bond.

As a result of our development of simple methods for the synthesis of mercuribisacetaldehyde [5] and the easy cleavage of this compound by alkali metals in liquid ammonia, the simplest metallic enolates, which have not been described previously, have now been made available.

In one of the first articles on reactions of monomercurized carbonyl compounds [2], we pointed out the probability of the formation of alcoholates of vinyl alcohol during the reaction of phenylmagnesium bromide with bromomercuriacetaldehyde according to the equation

$$BrHgCH_2CHO + C_6H_5MgBr \rightarrow C_6H_5HgBr + CH_2 = CHOMgBr.$$

Our unsuccessful attempts to carry out the symmetrization of $\alpha$-halomercuriketones by means of such symmetrizing agents as potassium iodide, sodium iodide, potassium thiocyanate, sodium thiosulfate, etc. [6] are also connected with the formation of enolates; in all of these cases, extremely ready hydrolysis of the Hg–C bond was observed in place of symmetrization.

At the present time, we consider that the cleavage of the Hg—C bond during attempts to symmetrize mercury salts of aldehydes and ketones by the action of various complex formers proceeds through the intermediate formation of the enolate:

$$ClHgCH_2CHO + 4NaI \rightarrow Na_2HgI_4 + NaCl + [CH_2 = CHONa].$$

The latter is readily hydrolyzed in aqueous medium, freeing the aldehyde (or, respectively, the ketone). The rupture of the Hg—C bond in esters of mercurized carboxylic acids proceeds under analogous conditions. $\sigma-\pi$—Conjugation, which is clearly expressed in the case of mercury derivatives of carbonyl compounds, permits cleavage of the Hg—C bond in these substances even with such weak complex formers as potassium chloride. Aqueous solutions of mercuribisacetaldehyde are completely decomposed by a 10% solution of potassium chloride, slowly in the cold and more rapidly on heating.

$$Hg(CH_2CHO)_2 + KCl \rightarrow ClHgCH_2CHO + [CH_2 = CHOK] \xrightarrow{H_2O} CH_3CHO + KOH.$$

The organomercury salt and the carbonyl compound resulting from this decomposition in alkaline medium give an amorphous, insoluble precipitate, as was previously found by Reynolds [7], Nef [8], and others.

For the formation of metallic derivatives of vinyl alcohol by an exchange reaction between a metal halide and the halomercuriacetaldehyde, we dispensed with an aqueous medium and carried out the reaction between anhydrous ferric chloride and chloromercuriacetaldehyde in dry acetone.

The structure and composition of the vinylate of ferric hydroxychloride $CH_2 = CHOFe(OH)Cl$, which was prepared by us by this method, was proved by analyses and by ozonation.*

Attempts at the alkylation and acylation of lithium and sodium vinylates under various conditions and with the aid of butyl bromide, allyl halides, dimethyl sulfate, benzoyl chloride, etc. were unsuccessful owing to the ready onset of vigorous tarring of the reaction mixture. This lack of success was evidently connected with the action of the vinylates of the alkali metals on the expected reaction products — aldehydes:

It was possible to liberate the halide salt in yields close to quantitative.

It may be supposed that the detailed investigation of the metallic derivatives of the simplest enol system, which will be continued by us, will yield important material for the further study of the problem of the conjugation of bonds and the transfer of the reactive center of the molecule.

## EXPERIMENTAL

Reaction of chloromercuriacetaldehyde with ferric chloride. To 14 g (0.05 mole) of chloromercuriacetaldehyde, which had been dried over $P_2O_5$ and carefully powdered, was added 20 ml of dry acetone and, with stirring, a solution of 2.8 g (0.017 mole) of anhydrous ferric chloride in 40 ml of acetone. The solution was filtered, and 200 ml of absolute ether was added to the filtered solution. The orange precipitate was separated, washed three times with ether, and twice reprecipitated with absolute ether from acetone solution. The resulting material corresponded in analysis to the vinylate of ferric hydroxychloride of the composition $CH_2 = CHOFe(OH)Cl$. The yield was 2.5 g (83% of theoretical). The material decomposed on heating, was readily hydrolyzed by water with the formation of acetaldehyde, and was soluble in acetone and pyridine.

Found %: C 15.60, 15.46; H 2.74, 2.65; Fe 35.7, 36.6. $CH_2 = CHOFe(OH)Cl$. Calculated %: C 15.80; H 2.64; Fe 36.6.

Ozonation of the vinylate of ferric hydroxychloride. The ozonation was carried out with a suspension of $CH_2 = CHOFe(OH)Cl$ (from 14 g of chloromercuriacetaldehyde and 2.8 g of anhydrous $FeCl_3$) in 40 ml of dry chloroform. After 2% ozone had been passed through the suspension for 14 hours at a rate of 4 liters/hour, all of the precipitate of iron vinylate was dissolved, and the solution acquired an orange color. The chloroform solution was poured into 50 ml of water which had been acidified with $H_2SO_4$ and which contained 0.5 g of $FeSO_4$. After complete decoloration of the chloroform solution, the aqueous extract was separated into two

*One atom of chlorine is apparently hydrolyzed by the water liberated by the partial condensation of acetone under the influence of the anhydrous ferric chloride.

parts. To the first part was added a saturated aqueous solution of 1.5 g of dimedone. After 2 hours, 0.4 g of the dimedone derivative of formaldehyde, m. p. 189° (recrystallized twice from alcohol), was isolated. Literature data [9]: m. p. 189°. The second part of the aqueous solution was neutralized with soda and evaporated to dryness; heating of the dry residue with an aqueous-alcoholic solution of p-chlorophenacyl bromide gave the p-chlorophenacyl ester of formic acid, m. p. 127-127.5°. Literature data [10]: m. p. 128°.

Preparation of sodium vinylate. To a solution of 3 g of sodium in 120 ml of liquid ammonia, mercuribisacetaldehyde was added in small portions and with vigorous stirring precisely until the blue color of the solution disappeared; this required about 13.7 g of the mercury compound (even a small excess of the mercuribisacetaldehyde causes tarring of the reaction mixture). Careful protection of the reaction mixture from atmosphere moisture and carbon dioxide was required in all operations. The reaction mixture was centrifuged, and the solution was decanted from the amalgam and filtered through a fine porous glass filter. After evaporation of the ammonia, the white, crystalline residue was dried for several hours under vacuum. The yield of sodium vinylate was 5 g (80% of theoretical).

Found %: C 35.69, 35.20; H 4.76, 4.71; Na 35.6. $CH_2 = CHONa$. Calculated %: C 35.35; H 4.58; Na 34.8.

Preparation of lithium vinylate. Under conditions analogous to those described above, 14.3 g of mercuribisacetaldehyde and 1 g of lithium in 120 ml of liquid ammonia gave 3.8 g (78% of theoretical) of lithium vinylate as a white, crystalline material. The lithium vinylate was soluble in benzene and ether.

Found %: C 47.68, 47.70; H 6.67, 6.67. $CH_2 = CHOLi$. Calculated %: C 48.03; H 6.05.

Hydrolysis of lithium vinylate. To 300 ml of a saturated aqueous solution of dimedone was added 10 ml of a 1 N solution of sulfuric acid and then 0.3 g of lithium vinylate. After several days, 1 g (60% of theoretical) of the dimedone derivative was separated, m. p. 136°. A mixture of this material with the dimedone derivative of acetaldehyde showed no melting point depression. Literature data [9]: m. p. 138°.

## LITERATURE CITED

[1] A. N. Nesmeianov, I. F. Lutsenko and N. N. Vereshchagina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1947, 63.

[2] A. N. Nesmeianov and I. F. Lutsenko, Proc. Acad. Sci. USSR, 59, 707 (1948).

[3] A. N. Nesmeianov, I. F. Lutsenko and Z. M. Tumanova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1949, 601.

[4] A. N. Nesmeianov and E. G. Perevalova, Bull. Acad. Sci. USSR, 1954, 1002.

[5] I. F. Lutsenko and R. M. Khomutov, Proc. Acad. Sci. USSR, 102, 97 (1955).

[6] A. N. Nesmeianov, I. F. Lutsenko and R. M. Khomutov, Proc. Acad. Sci. USSR, 88, 837 (1953).

[7] J. Reynolds, Ber. 4, 483 (1871).

[8] J. Nef, Lieb. Ann. 298, 316 (1898).

[9] D. Vorländer, Zs. anal. Chem. 77, 31 (1929).

[10] C. Moses, J. Am. Chem. Soc. 54, 2101 (1932).

M. V. Lomonosov Moscow
State University

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# THE STEREOCHEMISTRY OF ISOTOPE EXCHANGE REACTIONS OF ORGANOMERCURY SALTS WITH METALLIC MERCURY AND MERCURY HALIDE LABELED WITH $Hg^{203}$

O. A. Reutov, P. Knoll' and U Ian-Tsei

(Presented by Academician A. N. Nesmeianov, February 26, 1958)

In the course of a study of the mechanism of isotope exchange between organomercury compounds and metallic mercury or mercury halide [1-4], clarification of the stereochemisty of the following reactions became necessary:

$$R_1R_2R_3C-HgX+\overset{*}{Hg}\rightleftarrows R_1R_2R_3C-\overset{*}{Hg}X+Hg \tag{1}$$

$$R_1R_2R_3C-HgX+\overset{*}{Hg}X_2\rightleftarrows R_1R_2R_3C-\overset{*}{Hg}X+HgX_2 \tag{2}$$

Reaction (1) is an homolytic process, while Reaction (2) is one of electrophilic substitution at a saturated carbon atom.

The present article describes the results of a study of the stereochemistry of Reaction (1), using the L-menthyl esters of $\alpha$-bromomercuriphenylacetic acid as the organomercury compound, and of Reaction (2), using the cis- and trans-isomers of 2-methoxycyclohexylmercury chloride.

Both of the diastereoisomers of the L-menthyl ester of $\alpha$-bromomercuriphenylacetic acid ((I) with $[\alpha]_D^{18}-86°\pm 2$ and (II) with $[\alpha]_D^{18}-49°\pm 2$) readily react with finely dispersed metallic mercury in the cold in absolute benzene. In both cases, complete retention of the stereochemical configuration at the $\alpha$-carbon atom was definitely established: the angles of rotation of the diastereoisomers before the reaction and after the establishment of isotopic equilibrium were identical.

$$\underset{\substack{|\\ HgBr}}{C_6H_5-CH-COOC_{10}H_{19}}+\overset{*}{Hg}\rightleftarrows \underset{\substack{|\\ \overset{*}{Hg}Br}}{C_6H_5-CH-COOC_{10}H_{19}}+Hg$$

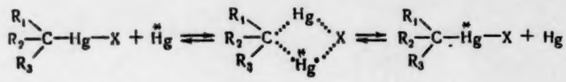
(I) $[\alpha]_D^{18}-86°\pm 2$ $\qquad$ $[\alpha]_D^{18}-85{,}7°\pm 2$

$$\underset{\substack{|\\ HgBr}}{C_6H_5-CH-COOC_{10}H_{19}}+\overset{*}{Hg}\rightleftarrows \underset{\substack{|\\ \overset{*}{Hg}Br}}{C_6H_5-CH-COOC_{10}H_{19}}+Hg$$

(II) $[\alpha]_D^{18}-52°\pm 2$ $\qquad$ $[\alpha]_D^{18}-49{,}6°\pm 2$

The retention of stereochemical configuration at the saturated carbon atom during isotope exchange reactions between organomercury salts and radioactive metallic mercury is needless evidence in support of the proposition that these homolytic reactions are not free radical reactions, since in the event of the intermediate formation of free radicals, $R_1R_2R_3C$, the stereochemical result of these reactions would be racemization.

The molecules of the organomercury compounds apparently react directly with the mercury molecules: *

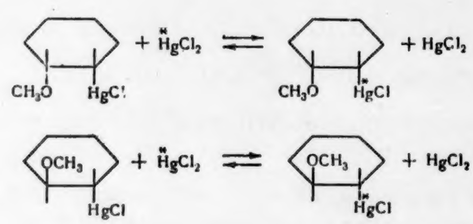


The diastereoisomeric L-menthyl esters of $\alpha$-bromomercuriphenylacetic acid were unsuitable for the clarification of the stereochemistry of the isotope exchange reaction with mercury halide, since mercuric bromide causes rapid "racemization" of both diastereoisomers (at the $\alpha$-carbon atom) even under conditions so mild that isotope exchange does not occur.

In this connection, cis- and trans-2-methoxycyclohexylmercury halides were selected as subjects for the study of the reaction with mercury halide. The melting points of the cis- (114°) and trans-isomers (115°) differ very little; however, the melting point of a mixture of the cis- and trans-isomers (~85°) is greatly depressed. This circumstance considerably facilitates identification of both isomers.

The isotope exchange reaction was carried out in dioxane, acetone, and isobutyl alcohol. Isotope exchange proceeded at an appreciable rate only at temperatures of 120-135°. **

In all cases, strict retention of the original stereochemical configuration of the materials was definitely established:



Thus, this isotope exchange reaction, which is a process of electrophilic substitution at a saturated carbon atom, proceeds with retention of configuration. It should be noted that this same result has been definitely established for all other investigated reactions of electrophilic substitution at a saturated carbon atom with the exception of the cases reported by Cram [5].

## EXPERIMENTAL

Interaction of diastereoisomer (I) ($[\alpha]_D^{18}$ − 86°) of the L-menthyl ester of $\alpha$-bromomercuriphenylacetic acid with metallic mercury labeled with $Hg^{203}$. A solution in 60 ml of absolute benzene of 0.50 g ($9 \cdot 10^{-4}$ mole) of the diastereoisomer of the L-menthyl ester of $\alpha$-bromomercuriphenylacetic acid with $[\alpha]_D^{18}$ − 86° and a m. p. of 153° (0.015 mole/liter concentration) and 20 g of metallic mercury (111-fold g-equivalent excess) labeled with $Hg^{203}$ were vigorously stirred (Witt stirrer at 2500 ± 200 rpm) in the cold for 15 hours. At the conclusion of the reaction, the metallic mercury was filtered. In order to free the solution from colloidal mercury, it was passed through a chromatographic column packed with aluminum oxide. The solution was then evaporated in the cold under a stream of dry air. The dry residue, which weighed 0.46 g, was dissolved by heating in the minimum amount of carbon tetrachloride, several drops of methyl alcohol were then added to

* The alternate mechanism

$$R_1R_2R_3C-HgX + \overset{*}{Hg} \rightleftharpoons R_1R_2R_3C-Hg-\overset{*}{Hg}-X \rightleftharpoons R_1R_2R_3C-\overset{*}{Hg}-X + Hg$$

seems less probable to us.

** Under these conditions, along with exchange, decomposition of the starting materials with the formation of calomel proceeds to an appreciable extent.

the solution, and the solution was cooled to $-10°$. The material was crystallized by rubbing the wall of the vessel with a glass rod. The weight was 0.35 g (70% of theoretical). M. p. 153-154°; $[\alpha]_D^{18} = 85.7° \pm 2$ ($C = 0.854$; $l = 1.9$; $\alpha = 0.95° \pm 0.02$).*

Measurement of the radioactivity of the preparation showed that there was 100% exchange, i.e., the activity of the preparation was equilibrium activity.

The results of parallel experiments on the interaction of diastereoisomer (I) with radioactive metallic mercury were in good agreement.

Interaction of diastereoisomer (II) ($[\alpha]_D^{18} - 52°$) of the L-menthyl ester of $\alpha$-bromomercuriphenylacetic acid with metallic mercury labeled with $Hg^{203}$. A solution in 42 ml of absolute benzene of 0.35 g ($6.3 \cdot 10^{-4}$ mole) of the diastereoisomer of the L-menthyl ester of $\alpha$-bromomercuriphenylacetic acid with $[\alpha]_D^{18} - 52°$ and a m. p. of 144-146° (0.015 mole/liter concentration) and 20 g of metallic mercury (159-fold g-equivalent excess) labeled with $Hg^{203}$ were vigorously stirred in the cold for 15 hours. The mercury was filtered, the filtrate was passed through a column packed with aluminum oxide, and the solvent was then evaporated in the cold. The dry residue weighed 0.32 g. After recrystallization from carbon tetrachloride, as in the preceding experiment, the weight of the material was 0.24 g (68% of theoretical). M. p. 145-146°; $[\alpha]_D^{18} - 49.6° \pm 2°$ ($C = 0.584$; $l = 1.9$; $\alpha = -0.55° \pm 0.02°$). Measurement of the radioactivity of the preparation showed that there was 100% exchange.

Interaction of trans-2-methoxycyclohexylmercury chloride with calomel labeled with $Hg^{203}$. Solutions containing equimolar amounts of trans-2-methoxycyclohexylmercury chloride and calomel, the latter labeled with $Hg^{203}$, were held for specific lengths of time at constant temperature in sealed tubes or in an apparatus fitted with a reflux condenser. At the conclusion of the reaction, the solvent was evaporated in the cold, and the trans-2-methylcyclohexylmercury chloride was extracted from the residue with cold carbon tetrachloride. Before measurement of the radioactivity and determination of the melting point, the material was twice crystallized from methyl alcohol. The results of our experiments are presented in Table 1.

TABLE 1

| Expt. No. | Molar concentration of reacting substances | Reaction temp. °C | Solvent | Exchange time, hours | Activity of preparation, imp/min · · mg Hg | Equilibrium activity, imp/min · · mg Hg | % exchange |
|---|---|---|---|---|---|---|---|
| 1 | 0.05 | 23 | Acetone | 25 | 5 | 1140 | 0 |
| 2 | 0.05 | 50 | " | 6 | 95 | 2520 | 4 |
| 3 | 0.1 | 98 | " | 0.5 | 30 | 486 | 6 |
| 4 | 0.1 | 98 | " | 1.0 | 32 | 486 | 7 |
| 5 | 0.1 | 98 | " | 2.0 | 6 | 486 | 1 |
| 6 | 0.1 | 135 | " | 0.5 | 77 | 1400 | 6 |
| 7 | 0.1 | 135 | " | 1.5 | 178 | 1400 | 13 |
| 8 | 0.1 | 135 | " | 3.0 | 284 | 1400 | 20 |
| 9 | 0.1 | 120 | Dioxan | 9.5 | 1250 | 1900 | 66 |
| 10 | 0.1 | 130 | " | 3.0 | 1095 | 1900 | 58 |

*Experiments Nos. 3-10 were carried out in sealed tubes.

Determination of the melting points of the 2-methoxycyclohexylmercury chloride isolated after the reaction, and its mixtures with known samples of the cis- and trans-isomers, gave, in all experiments, the following identical results: the substance isolated after the reaction melted at 113°, i.e., the same as before the reaction; a mixture of the material with the cis-isomer melted at 84-86°; a mixture of the material with known trans-isomer melted at 112-113°.

Interaction of cis-2-methoxycyclohexylmercury chloride with calomel labeled with $Hg^{203}$. The isotope exchange reaction and the isolation of the product were carried out just as in the case of the trans-isomer. The experimental results are presented in Table 2.

*It was shown by means of special experiments with a known mixture of the diastereoisomers consisting of 70% (I) and 30% (II) that the treatment used in the experiment could not result in separation of the mixture with the isolation of pure (I).

TABLE 2

| Expt. No. | Molar conc. of reacting substances | Reaction temp., °C | Solvent | Exchange time, hours | Activity of preparation, imp/min · mg Hg | Equilibrium activity, imp/min · mg Hg | % exchange |
|---|---|---|---|---|---|---|---|
| 1 | 0.01 | 80 | Isobutyl alcohol | 4 | 18 | 2360 | 1 |
| 2 | 0.05 | 80 | Same | 8 | 24 | 486 | 5 |
| 3 | 0.05 | 80 | | 16 | 28 | 486 | 6 |
| 4 | 0.1 | 120 | Dioxane | 9.5 | 147 | 1900 | 8 |
| 5 | 0.1 | 130 | | 10 | 1205 | 1900 | 63 |

Determination of the melting points of the 2-methoxycyclohexylmercury chloride isolated after the reaction and its mixtures with known samples of the cis- and trans-isomers, gave, in all experiments, the following identical results: the substance isolated from the reaction mixture melted at 112°; a mixture of the material with known cis-isomer melted at 112-113°; a mixture of the material with known trans-isomer melted at 84-85°.

## LITERATURE CITED


[1] O. A. Reutov and G. M. Ostapchuk, Proc. Acad. Sci. USSR, 117, No. 5 (1957).*

[2] O. A. Reutov and U Ian-Tsei, Proc. Acad. Sci. USSR, 117, No. 6 (1957).*

[3] O. A. Reutov, G. M. Ostapchuk, U Ian-Tsei, T. A. Smolina and P. Knoll', Trans. of the All-Union Scientific-Technical Conference on the Use of Radioactive and Stable Isotopes and Radiation in the National Economy and Sciences, Izd. AN SSSR, 1958.**

[4] O. A. Reutov, T. A. Smolina, U Ian-Tsei and Iu. N. Bubnov, Reports of the Supreme School, No. 2 (1958).**

[5] D. Cram, Congress Handbook 14th International Congress of Pure and Applied Chemistry, Zürich, 5955, S. 39.



M. V. Lomonosov Moscow
State University



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** In Russian.

# UNSATURATED HYDROCARBONS IN A THERMALLY CRACKED GASOLINE

Academician A. V. Topchiev, I. A. Musaev, Z. Kh. Iskhakova, A. N. Kislinskii and G. D. Gal'pern

In our preceding communications we have reported on the chemical composition of thermally cracked gasoline fractions boiling up to 60° from Grozny paraffinic petroleum [1] and on the development of a chromatographic method for the separation of mixtures consisting of naphthenic-paraffinic, olefinic, and aromatic hydrocarbons [2]. By means of the proposed method, we separated the 60-150° fraction of this same gasoline into naphthenic-paraffinic, olefinic, and aromatic hydrocarbon fractions. We have also reported previously on the composition of the aromatic and hexamethylene fractions separated from the 60-150° fraction of the gasoline [3].

In the present communication, we present data on the hydrocarbon composition of the olefinic part of this fraction. The olefinic fraction was distilled into 10 narrow fractions in a column of 45 theoretical plates; the characteristics of these fractions are presented in Table 1.

TABLE 1

| Fraction No. | Cut points (°C/760) | Yield of fractions (g) | Yield of fractions (%) of olefinic fraction | of 60-150° gasoline | of 150° e. p. gasoline | $n_D^{20}$ | $d_4^{20}$ | Iodine No. | Mol. wt. | Max. aniline point |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 60–66 | 15.07 | 6.97 | 2.67 | 2.44 | 1.3939 | 0.6902 | 295.9 | 82.9 | 22.5 |
| 2 | 66–80 | 20.99 | 9.91 | 3.72 | 3.40 | 1.4100 | 0.7196 | 305.0 | 84.1 | 15.1 |
| 3 | 80–90 | 9.39 | 4.34 | 1.66 | 1.52 | 1.4098 | 0.7225 | 272.3 | 95.8 | 24.9 |
| 4 | 90–98 | 32.78 | 15.16 | 5.81 | 5.31 | 1.4118 | 0.7232 | 274.0 | 96.4 | 25.7 |
| 5 | 98–110 | 18.66 | 8.63 | 3.30 | 3.02 | 1.4387 | 0.7868 | 305.0 | 94.9 | 8.4 |
| 6 | 110–120 | 16.51 | 7.63 | 2.92 | 2.67 | 1.4249 | 0.7538 | 261.0 | 107.4 | 25.2 |
| 7 | 120–123 | 17.81 | 8.24 | 3.15 | 2.88 | 1.4230 | 0.7462 | 283.5 | 109.1 | 28.9 |
| 8 | 123–137 | 27.60 | 12.76 | 4.89 | 4.47 | 1.4370 | 0.7803 | 285.0 | 111.3 | 22.5 |
| 9 | 137–144 | 17.52 | 8.10 | 3.10 | 2.84 | 1.4347 | 0.7751 | 270.2 | 122.4 | 29.8 |
| 10 | 144–150 | 23.81 | 11.01 | 4.22 | 3.86 | 1.4360 | 0.7786 | 245.0 | 122.5 | 31.1 |
| | Residue 150 | 16.1 | 7.45 | 2.85 | 2.61 | — | — | — | — | — |
| | Total . . . | 216.24 | 100.0 | 38.29 | 35.02 | — | — | — | — | — |

Note: Fractions Nos. 1 and 2) $C_6$, Nos. 3, 4, and 5) $C_7$, Nos. 6, 7, and 8) $C_8$, Nos. 9 and 10) $C_9$.

The molecular weights (Table 1) show that the fractions were divided among 4 groups according to the number of carbon atoms in the molecule.

Judging from its characteristics, the 5th fraction apparently consisted mainly of cycloolefins. The detailed group composition of the fractions was investigated using the sulfuric acid method, catalytic hydrogenation and dehydrogenation, and aniline points.

TABLE 2

| Fraction No. | Boiling range (°C) | Content in fraction (wt. %) cyclo-hexenes | cyclo-pentenes | alkenes |
|---|---|---|---|---|
| 1 | 60—66 | 0 | 29 | 80 |
| 2 | 66—80 | 4 | 38 | 58 |
| 3* | 80—90 | 25 | 0 | 75 |
| 4 | 90—98 | 3 | 29 | 68 |
| 5 | 98—110 | 29 | 61 | 10 |
| 6 | 110—120 | 12 | 30 | 58 |
| 7 | 120—123 | 0 | 35 | 65 |
| 8 | 123—137 | 28 | 41 | 31 |
| 9 | 137—144 | 13 | 32 | 55 |
| 10 | 144—150 | 18 | 37 | 45 |
| Total | 60—150° | 13.2 | 32.3 | 54.5 |

* The contents of cyclopentenes and cyclohexenes in Fraction No. 3 were determined by an optical method.

TABLE 3

Unsaturated Hydrocarbons Found in Thermally Cracked Gasoline and Their Concentration in 150 E. P. Gasoline

| Olefins | Content in 150 e.p. gasoline (wt. %) | Cycloolefins | Content in 150 e.p. gasoline (wt. %) |
|---|---|---|---|
| 1-Hexene | 1.71 | 3-Methyl-1-cyclopentene | 0.37 |
| 2-Methyl-2-pentene | 1.38 | 1-Methyl-1-cyclopentene | 1.02 |
| 3-Methyl-2-pentene | 0.17 | Cyclohexene | 0.55 |
| | 1.02 | Total $C_6H_{10}$ | 1.94 |
| Total $C_6H_{12}$ | 4.28 | Methylcyclohexenes | 1.47 |
| 2-Methylhexenes | 0.90 | 1,2-Dimethylcyclopentenes | 2.19 |
| 1- and 2-heptenes (1-heptene predominated) | 2.69 | 1,3-Dimethylcyclopentenes | 1.06 |
| Unresolved | 1.14 | Ethylcyclopentenes | 0.15 |
| Total $C_7H_{14}$ | 4.73 | Total $C_7H_{12}$ | 4.87 |
| 2-Methylheptenes | 1.65 | 1,1-Dimethylcyclohexenes | 0.27 |
| 2,2- and 3,4-Dimethylhexenes | 0.26 | 1,2,3-Trimethylcyclopentenes 1,2,4-Trimethylcyclopentenes | 3.58 |
| n-Octenes | 2.04 | Ethylcyclohexenes | 0.59 |
| Total $C_8H_{16}$ | 3.95 | 1,2-Dimethylcyclohexenes | 0.42 |
| $C_9$-Olefins ($C_9H_{18}$) | 3.75 | 1,3-Dimethylcyclohexenes | 0.54 |
| Total $C_6$-$C_9$ alkenes | 16.71 | 1,4-Dimethylcyclohexenes | 0.22 |
| Structural groups: | | Total $C_8H_{14}$ | 5.62 |
| Normal olefins | 7.46 | 1,2,4-Trimethylcyclohexenes | 0.23 |
| With one branch | 4.10 | 1-Methyl-2-ethylcyclohexenes | 0.46 |
| With two branches | 0.26 | 1,1,3-Trimethylcyclohexenes | 2.40 |
| $C_9$-olefins | 3.75 | Total $C_9H_{16}$ | 1.14 |
| | | Total $C_6$-$C_9$ cyclenes | 13.57 |
| | | Structural groups: | |
| | | Without substituents | 0.55 |
| | | With one substituent | 3.77 |
| | | With two substituents | 5.30 |
| | | With three substituents | 2.70 |
| | | Unresolved | 2.40 |

As seen from Table 2, the content of cyclopentene hydrocarbons predominated considerably over the cyclohexenes in all fractions (Fractions Nos. 1, 2, 4, and 7 were practically devoid of cyclohexene hydrocarbons).

The cyclenes were distributed irregularly through the fractions. Thus, in Fractions Nos. 8 and 10, the cyclene content exceeded the alkene content, the cyclene contents of these fractions being, respectively, 69 and 55%. Fraction 5 was especially rich in cyclenes, containing 90%.

The individual hydrocarbon composition of the fractions was investigated by means of Raman spectra. The method and equipment used were the same as used in the determination of the composition of the fraction of this gasoline boiling up to 60° [1].

For the most complete resolution of the fractions, the spectra of the initial olefinic fractions and the spectra of these fractions after hydrogenation and, beginning with Fraction No. 7, also after dehydrogenation, were investigated. The Raman spectra catalog [4] and other literature data [5-11] were used in the interpretation of the spectra. By means of the above-mentioned method, we were able to decipher the individual hydrocarbon compositions of the first five fractions (to 110°). In the higher-boiling fractions (110-150°), only the carbon skeletons of the olefins were determined without indicating the positions of the double bonds in the molecules.

The total data on the individual hydrocarbon composition of the unsaturates, separated from the 60-150° fraction of the thermally cracked gasoline, are presented in Table 3.

As seen from Table 3, the aliphatic olefins are represented mainly by unbranched and slightly branched olefins, and the cyclenes by mono- and disubstituted compounds. Diolefins and olefins with quaternary carbon atoms were not found. They are apparently not present in this gasoline, or their amounts lie beyond the limits of determination by spectral analysis. No saturated hydrocarbons were detected in the olefinic fractions.

## LITERATURE CITED


[1] A. V. Topchiev, I. A. Musaev, et al., Chem. and Technology of Fuels and Oils, No. 12, 1 (1956).*

[2] A. V. Topchiev, E. Kh. Iskhakova, et al., Ibid, No. 11, 26 (1957).*

[3] A. V. Topchiev, I. A. Musaev, et al., Proc. Acad. Sci. Azer. SSSR, 14, No. 4, 291 (1958).

[4] G. S. Landsberg, P. A. Bazhulin and M. M. Sushchinskii, Basic Parameters of the Raman Spectra of Hydrocarbons,* Izd. AN SSSR, 1956.*

[5] W. G. Braun, D. F. Spooner and M. R. Fenske, Anal. Chem. 22, 1074 (1950).

[6] E. G. Treshchova, P. A. Akishin and V. M. Tatevskii, J. Anal. Chem. 3, No. 2, 75 (1948).

[7] V. T. Aleksanian, M. Iu. Lukina, Kh. E. Sterin and B. A. Kazanskii, Bull. Acad. Sci. USSR, Series Physics, 18, No. 6,699 (1954).

[8] H. Landolt and R. Börnstein, Physikalisch-chemische Tabellen, 1,Teil 2; 1, Teil 3, 1951.

[9] Catalog of Selected Raman Spectral Data (Project 44), Nat. Bur. of Stand., Washington, 1949.

[10] J. Goubeau, Beihefte zu der Angew. Chem. 56 (1949).

[11] G. Chiurdogdu, P. J. C. Fierens and C. Henkart, Bull. Soc. Chim. Belg. 59, 140 (1950).


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# MASS SPECTROMETRIC STUDY OF THE SUBLIMATION OF GERMANIUM DIOXIDE

S. A. Shchukarev and G. A. Semenov

(Presented by Academician A. N. Terenin, February 5, 1958)

The study of germanium compounds formed as surface films has attracted a great deal of attention, since the properties of this metal as a semiconductor depend to a great extent on the state of its surface. From this point of view, a knowledge of the thermodynamic characteristics of germanium dioxide, particularly the vapor pressure and heat of sublimation, is very essential, the more so since up to the present time these properties have not been generally studied.

Davydov [1], using the effusion method of Knudsen, measured the pressure of the saturated vapor over solid $GeO_2$. The heat of sublimation in the temperature ranges 886-980° and 1025-1078° was found to be 29.5 kcal/mole and 71.5 kcal/mole, respectively. The author ascribed this sharp change in the heat of sublimation to a phase transition at 1000°.

MS-1 and MS-4 type mass spectrometers were used in the execution of the present work. The ion source did not differ in principle from that described by Aldrich [2]. The germanium dioxide was placed on a platinum vaporizer, which consisted of a ribbon sealed by precision welding to a nichrome holder. The vapor was passed through a small hole into the ionization chamber, where it was ionized by electron impact. The temperature of the vaporizer was measured with a platinum–platinum-rhodium thermocouple sealed to the vaporizer.

In the source used by us, the value of the ion current was related to the vapor pressure of the material by the relationship [3]:

$$I^+ = \frac{kP}{T}.$$

The coefficient k depends on the geometry of the apparatus and on the effective ionization cross-section; therefore, the direct determination of k and, by the same token, of the vapor pressure of the material is difficult. Nevertheless, the heat of sublimation can be determined by measuring the dependence of the ion current on temperature and constructing a graph of log $(I^+ T)$ against f $\frac{1}{T}$ .

In preliminary experiments, we determined the value of the heat of sublimation of silver, for which numerous reliable data are available in the literature. According to our data, $\Delta H$ of sublimation in the interval 680-820 is equal to 66.5 ± 0.5 kcal/mole, which is in good agreement with the values 65.5 kcal/mole [4] and 68 kcal/mole [5]. Only the ion $Ag^+$ was detected in the mass spectrum of the silver vapors.

The germanium dioxide was prepared by dissolving metallic germanium in a nitric acid solution of hydrogen peroxide. The $GeO_2$ was then recrystallized from hot water.

In Table 1 are presented data on the mass spectrum of the vapor over $GeO_2$. The measurements were carried out at a vaporizer temperature of 1000°, an electron emission current of 1.5 ma., and three different ionization potentials. In compiling the table, we totaled the intensities of the ion currents corresponding to the separate germanium isotopes, and related them to the ion current of $Ge_3O_3^+$, the intensity of which was taken as unity.

TABLE 1

| Ionization potential, V | $Ge_3O_3^+$ | $Ge_2O_2^+$ | $Ge_2O^+$ | $GeO^+$ | $Ge^+$ | $O_2^+$ | $O^+$ |
|---|---|---|---|---|---|---|---|
| 70 | 1 | 1.15 | 0.3 | 0.95 | 0.56 | 2.6 | 0.15 |
| 40 | 1 | 0.85 | 0.22 | 0.55 | 0.3 | | |
| 15 | 1 | 0.48 | 0.13 | 0.42 | 0.19 | | |

We also detected the $Ge_3O_2^+$ and $GeO_2^+$ ions, the currents of which comprised about 0.5% of the current of $Ge_3O_3^+$. In Fig. 1 is presented the part of the mass spectrum corresponding to the groups of $Ge_2O_2^+$ and $Ge_3O_3^+$.

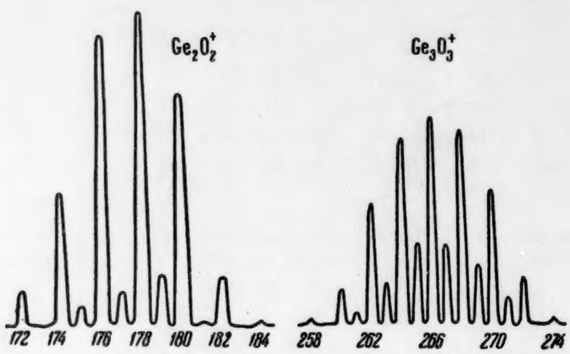


Fig. 1. Mass spectrum of the vapor over germanium dioxide.

For certain mass spectra groups, the dependence of the ion current intensities on temperature was measured (the measurements were carried out for the highest peak in the group). The enthalpy values (in kcal/mole), calculated from the slope of the straight lines log ($I^+$ T) against f $\frac{1}{T}$, were:

| Ion | $Ge^+$ | $GeO^+$ | $Ge_2O_2^+$ | $Ge_3O_3^+$ | $O_2^+$ | $O^+$ |
|---|---|---|---|---|---|---|
| $\Delta H_T$ | $106\pm5$ | $101\pm2$ | $108\pm4$ | $113\pm5$ | 108 | 110 |

It was not possible to measure the temperature dependence of the $GeO_2$ ion current owing to the very low intensity.

Within the limits of error of our measurements, we did not observe any breaks in the curves of log ($I^+$ T) against f $\frac{1}{T}$. The magnitude of the vapor pressure of $Ge_3O_3$ can be calculated from a comparison of the ion currents of $Ge_3O_3^+$ and $Ag^+$. The ratio of the ionization cross-sections of the molecule $Ge_3O_3$ and the Ag atom is close to 4:1 [6]. Whereupon, we may assume:

$$I_1^+ T_1 = \frac{I_2^+ T_2}{4} = kP,$$

where $I_1^+T_1$ and $I_2^+T_2$ are related to the ion currents of $Ag^+$ and $Ge_3O_3^+$, respectively. This equality held for our ion source at, for example $T_1 = 1073°$ and $T_2 = 1338°$. The vapor pressure of silver at 800° is $6\cdot10^{-5}$ mm Hg [4, 5]. Consequently, the vapor pressure of $Ge_3O_3$ at a temperature of 1065° is approximately of the order of $2\cdot10^{-5}$ mm Hg.

Thus, with respect to the composition of the gas phase, the vaporization of germanium dioxide is analogous to the case of $SiO_2$ [7, 8], where chiefly molecules of SiO are observed in the vapors. The stability of GeO toward disproportionation has been previously demonstrated by calculation [9].

## LITERATURE CITED


[1] V. I. Davydov, J. Inorg. Chem. 2, 1460 (1957).

[2] L. T. Aldrich, J. Appl. Phys. 22, 1168 (1951).

[3] M. G. Inghram and W. A. Chupka, J. Chem. Phys. 21, 371 (1953).

[4] C. L. McCabe and C. E. Birchenall, J. Metals, 197, 707 (1953).

[5] Iu. V. Kornev and E. Z. Vintaikin, Proc. Acad. Sci. USSR, 107, 661 (1956).*

[6] W. A. Chupka and M. G. Inghram, J. Phys. Chem. 59, 100 (1955).

[7] L. Brewer and R. K. Edwards, J. Phys. Chem. 58, 351 (1954).

[8] R. F. Porter, W. A. Chupka and M. G. Inghram, J. Chem. Phys. 23, 216 (1955).

[9] S. A. Shchukarev, Bull. Leningrad State Univ. No. 11, 127 (1954).



A. A. Zhdanov Leningrad
State University



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THE EFFECT OF SILICON ON THE SOLUBILITY OF OXYGEN IN IRON-CHROMIUM MELTS

V. V. Averin and Corresponding Member AN SSSR A. M. Samarin

The present communication reports the results of an experimental study of the effect of silicon (up to 1.5%) on the solubility of oxygen in liquid iron-chromium melts at 1600°.

The method of investigation has been previously described [1, 2]. The attainment of equilibrium was determined by the distinct appearance of an oxide phase on the surface of the liquid metal. After equilibrium had been established, samples of the metal were collected, the composition of the metal being varied by the introduction of chromium and silicon. The experimental results are presented in Fig. 1.

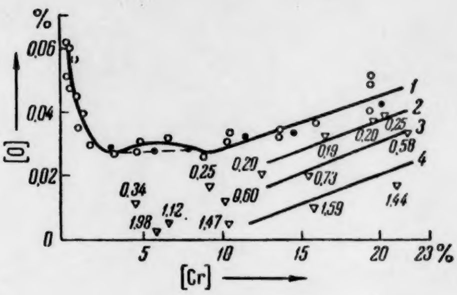


Fig. 1. The effect of silicon on the solubility of oxygen in iron-chromium melts at 1600°. The solid points mark the results of determinations of the concentration of oxygen in an Fe–Cr–Ni alloy (10% Ni). Figures at the points indicate the silicon concentration; 1) 0% Si, 2) 0.2% Si, 3) 0.5% Si, 4) 1.5% Si.

On the basis of the data of Fig. 1, the following conclusions may be formulated:

1. The experimentally determined solubility of oxygen in the iron-chromium melts, is in good agreement with previously published data [3, 4].

2. The addition of nickel (10%) to the iron-chromium melts does not result in a change in the solubility of oxygen. This indicates that it is possible to evaluate the limiting solubility of oxygen in stainless steels by a study of the solubility in binary systems of chromium and iron. The addition of nickel leads to a smooth change in the concentration of oxygen with a change in the iron-chromium ratio. Apparently, this is explained by a change in the structure of the oxides formed in the chromium content interval of 3 to 10%. According to literature data [4], spinels with a deformed lattice are formed at these chromium concentrations in the iron-chromium system.

3. The presence of silicon decreases the solubility of oxygen in iron-chromium melts.

4. The presence of chromium leads to a significant decrease in the deoxidizing properties of silicon in iron-chromium melts. Thus, at 18% Cr and 0.80% Si in the melt, in spite of a decrease in the oxygen content by a factor of two, the residual concentration of oxygen is 0.020% as against an oxygen concentration of 0.005% for iron with the same silicon content.

5. At constant chromium content (greater than 10% Cr), with an increase in the silicon concentration there is a decrease in the reducing power of the silicon. At 18% Cr and 1600°C, the relationship between the residual oxygen concentration and the silicon content is given by the equation $\log [\%\,O] = -0.40\,[\%\,Si] - 1.38$.

6. In the range of silicon concentrations studied (0.2-1.5% Si), the equilibrium oxide phase appearing as a result of the interaction of the gas mixture with the liquid metal consists basically of silica.

## LITERATURE CITED

[1] V. V. Averin, A. Iu. Poliakov and A. M. Samarin, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 3, 90 (1955).*

[2] V. V. Averin, A. Iu. Poliakov and A. M. Samarin, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 11, 52 (1956).*

[3] B. V. Linchevskii and A. M. Samarin, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 5 (1953).*

[4] D. C. Hilty, W. D. Forgang and R. L. Folkman, J. Metals, No. 2 (1955).

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# THE EFFECT OF THE SOLVENT ON COORDINATION REACTIONS AND THE EFFECT OF "NEGATIVE COMPLEX FORMATIONS"

A. M. Golub

(Presented by Academician I. I. Chernaev, March 8, 1958)

It was previously shown [1] that in the presence of low concentrations of solvents such as alcohol, acetone, and dioxane, the nature of complex formation in aqueous systems remains the same as in pure aqueous solutions. A considerable increase in the concentrations of the nonaqueous solvents can change sharply the course of the complex formation reactions [2].

With the aim of clarifying the effect of high concentrations of the nonaqueous solvent on the complex formation reaction, we have studied the system $Cd^{2+} - CNS^- - H_2O$ –dioxane potentiometrically. Measurement of the e. m. f. was carried out with the following cell:

$$Cd(Hg) \mid Cd(NO_3)_2,\ H_2O,\ Dy \mid KNO_3 \mid Hg_2Cl_2,\ \underset{\text{sat.}}{KCl} \mid Hg.$$

where Dy indicates dioxane and Cd(Hg) is cadmium amalgam, which served as the indicator electrode. The concentration of the cadmium salts in the mixtures investigated was constant (0.01 M). Three series of experiments were carried out: at dioxane concentrations in the mixtures of 2.5, 5 and 7.5 molar. The investigation was carried out at a temperature of 20° ± 0.05°. The results of the potentiometric measurements (see Tables 1-3 and Fig. 1) were treated as in the works cited above.

TABLE 1

Results of the Potentiometric Study of the System $Cd^{2+}-CSN^- - H_2O-Dy$ at a Dioxane Concentration of 2.5 M.

| Concentration of KCNS | E (v) | lg [$Cd^{2+}$] | $K_3 \cdot 10^4$ | $K_4 \cdot 10^4$ |
|---|---|---|---|---|
| | −0.6404 | −2.000 | — | — |
| 0.3657 | −0.6964 | −3.9310 | 5.26 | — |
| 0.4876 | −0.7060 | −4.2621 | 6.88 | — |
| 0.7314 | −0.7187 | −4.7010 | 7.86 | — |
| 0.9752 | −0.7283 | −5.0310 | 8.23 | — |
| 1.2190 | −0.7364 | −5.3103 | 6.20 | 9.46 |
| 1.4628 | −0.7470 | −5.6759 | — | 8.65 |
| 1.7066 | −0.7543 | −5.9276 | — | 9.13 |
| 1.9504 | −0.7606 | −6.1448 | — | 9.53 |
| 2.1942 | −0.7669 | −6.6327 | — | 9.33 |
| | | Average. . . | $6.67 \pm \pm 0.46 \cdot 10^{-4}$ | $9.26 \pm \pm 0.15 \cdot 10^{-4}$ |

Before beginning the investigation of the solutions, we attempted to clarify how dioxane behaves toward cadmium salts, which, in general, dissociate very readily. It was established that cadmium nitrate and perchlorate are readily soluble in dioxane. We isolated the molecular compounds $Cd(NO_3)_2 \cdot 2Dy$ and $Cd(ClO_4)_2 \cdot 2Dy$ in the form of colorless crystals from saturated solutions of cadmium nitrate and perchlorate.

TABLE 2

Results of the Potentiometric Study of the System $Cd^{2+}-CNS^{-}-H_2O-Dy$ at a Dioxan Concentration of 5 M

| Concn. of KCNS | E (v) | $\lg[Cd^{2+}]$ | $K_3 \cdot 10^4$ | $K_4 \cdot 10^4$ | $K_6 \cdot 10^4$ |
|---|---|---|---|---|---|
| — | —0.6399 | —2.000 | | | |
| 0.4884 | —0.7212 | —4.8034 | 1.52 | | |
| 0.7326 | —0.735 | —5.3034 | 1.73 | | |
| 0.9768 | —0.7470 | —5.6931 | 1.72 | | |
| 1.2210 | —0.7558 | —5.9966 | 1.70 | 1.96 | |
| 1.4652 | —0.7648 | —6.3069 | | 2.03 | |
| 1.7094 | —0.7730 | —6.5847 | | 2.02 | 5.27 |
| 1.9536 | —0.7830 | —6.9345 | | | 5.37 |
| 2.1978 | —0.7907 | —7.2000 | | | 6.03 |
| | | Average. . . | $1.67 \pm 0.05 \cdot 10^{-4}$ | $2.00 \pm 0.03 \cdot 10^{-4}$ | $5.5610 \pm 0.20 \cdot 10^{-4}$ |

From this, it would be expected that cadmium ions are capable of combining with dioxane in the presence of water to form complexes. But since the concentration of dioxane was constant in each series of experiments, this should not interfere with the determination of the composition of the thiocyanate complexes of cadmium.

TABLE 3

Results of the Potentiometric Study of the System $Cd^{2+}-CNS^{-}-H_2O-Dy$ at a Dioxane Concentration of 7.5 M

| Concn. of KCNS | E (v) | $\lg[Cd^{2+}]$ | $K_6 \cdot 10^5$ |
|---|---|---|---|
| — | —0.6308 | —2.000 | |
| 1.195 | —0.7772 | —7.0483 | 1.84 |
| 1.434 | —0.7882 | —7.4276 | 2.51 |
| 1.673 | —0.7941 | —7.8034 | 2.77 |
| 1.912 | —0.8080 | —8.1000 | 3.19 |
| | | Average . . | $2,55 \pm 0.28 \cdot 10^{-5}$ |

In Tables 1-3 are presented the values of the dissociation constants of the complex, which is the dominant factor in the specific region of complex former concentration. The subscript at K indicates the number of thiocyanate ions entering into the composition of the corresponding complex.

Since proof of the higher coordination groups was more important to us, for the sake of brevity, data on solutions in which the simplest complexes are formed were omitted from the tables. As seen from Table 1 and Fig. 1, already at 2.5 moles of dioxane, it was considerably easier (on the score of concentration conditions) to detect the complex $Cd(CNS)_3^-$ than it is in aqueous solution, where the formation of this complex corresponds to 1-2 moles of KCNS [3] (under otherwise equivalent conditions). Moreover, in the mixed solution at 2.5 moles of dioxane, a more complicated complex was observed, namely $Cd(CNS)_4^{2-}$.

At higher concentrations of dioxane (see Tables 2 and 3) it was possible to detect not only the complex $Cd(CNS)_4^{2-}$, but also $Cd(CNS)_6^{4-}$. Thus, the introduction of dioxane increases the coordination potential of cadmium, for which a coordination number of 6 in anions is considered uncharacteristic. Moreover, at first glance, this is contradictory to the fact that molecular compounds are formed between cadmium salts and dioxane, because it is quite difficult to imagine that cadmium would

coordinate more thiocyanate ions in the presence of dioxane than in aqueous solution. In order to answer this question conclusively, we also carried out potentiometric measurements on the system $Cd^{2+}-H_2O-Dy$. The e.m.f. measurements in this case were carried out similarly to the above-described experiments at a constant concentration of $Cd(NO_3)_2$ (0.01 M) and with increasing concentrations of dioxane (0.1-6.5 M). The results of these measurements are presented in Table 4.

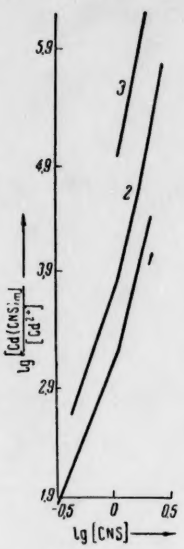


Fig. 1. Dependence of log $\frac{[Cd(CNS)m]}{[Cd^{2+}]}$ on log [CNS]. 1) At a dioxane concentration of 2.5 moles/liter, 2) at a dioxane concentration of 5 moles/liter, 3) at a dioxane concentration of 7.5 moles/liter.

As seen from Table 4, in place of the expected decrease in electrode potential values, which would indicate tying up of the cadmium ions in a complex, some increase in electrode potential was observed as the concentration of dioxane in the solution was increased. This provides a basis for the assertion that in aqueous solutions, complex groups of cadmium with dioxane are not formed. Further, tracing the change in electrode potential with increasing dioxane concentration, it may be said that so-called "negative complex formation" occurred, i.e., a tendency toward the formation of more free (in the sense of solvation) potential-determining ions. This is understandable if one takes into account the interaction of the nonaqueous solvent by hydrogen bonding with the water molecules which bond to the cadmium ions. If it is assumed that in the latter mixtures (Table 4) all cadmium ions are bound to dioxane molecules, and if one calculates the concentration of "free" (with decreased hydration) and "bound" (hydrated) cadmium ions by means of the decrease in e.m.f. from the last to the first mixture with an increase in the concentration of $H_2O$ in the mixture, then by constructing a graph of the relationship

$$\lg \frac{[Cd(H_2O)_{n+x}]}{[Cd(H_2O)_n]} = f(\lg [H_2O])$$

it is easy to find x – the change in the number of molecules of water grouped around the $Cd^{2+}$. With a change in the dioxane concentration of 6 M, even a very approximate calculation shows a decrease in the number of water molecules hydrating each cadmium. In the presence of ions which are capable of forming a complex with $Cd^{2+}$ ions, this dehydration must be appreciable.

TABLE 4

Changes in the Electrode Potential of Cadmium in the System $Cd^{2+}-H_2O-Dy$

| Dioxane concn. | E (v) | Dioxane concn. | E (v) |
|---|---|---|---|
| — | –0.6441 | 2.07 | –0.6397 |
| 0.23 | –0.6438 | 2.81 | –0.6388 |
| 0.69 | –0.6432 | 3.52 | –0.6360 |
| 0.92 | –0.6429 | 4.22 | –0.6346 |
| 1.38 | –0.6420 | 4.92 | –0.6312 |
| 1.61 | –0.6407 | 5.63 | –0.6274 |
| | | 6.33 | –0.6223 |

Considering this last effect, it is easy to explain the increase in the coordination number in cadmium complexes with an increase in the dioxane concentration in the solution, since dehydrated cadmium ions add thiocyanate ligands much more readily than do hydrated ions. It is possible to assume, therefore, that in aqueous solutions, $Cd^{2+}$ is surrounded by six water molecules. It is well known that even in the solid state cadmium perchlorate exists in the form $Cd(ClO_4)\cdot 6H_2O$ In the presence of an excess of thiocyanate ions, it is possible that the coordination sites are substituted (but not completely) by thiocyanate, whence it is possible to isolate the molecular salt $K_2Cd(CNS)_4\cdot 2H_2O$ [3, 4]. In mixed solutions in which there is a greater concentration of alcohol, acetone, or dioxane, each of which is capable of forming hydrogen bonds, the cadmium cations are more readily denuded, and in the region of

high concentrations of thiocyanate ions, the highest coordination complex $Cd(CNS)_6^{4-}$ will be formed, which is what is actually observed.

## LITERATURE CITED

[1] A. M. Golub, J. Gen. Chem. 26, No. 7, 1837 (1956).*

[2] A. M. Golub, Reports of the 7th All-Union Conference on the Chemistry of Complex Compounds, Leningrad, 1956, p. 36; Sci. Reports of the Kiev State Univ. Chem. Sect. No. 8, 41 (1957).

[3] A. M. Golub and O. G. Bilyk, J. Inorg. Chem. 2, No. 12, 1343 (1957);

[4] H. Grossmann, Ber. 35, 2668 (1902).

T. G. Shevchenko Kiev
State University

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# INVESTIGATION OF THE THERMAL TRANSFORMATIONS OF PHENOL UNDER HIGH HYDROGEN PRESSURES

M. G. Gonikberg and Li Guan-Nian'

(Presented by Academician B. A. Kazanskii, March 14, 1958)

Ipatieff and Orlov [1] and also Kling and Florentin [2, 3] pointed out the high thermal stability of phenol at 500°. Only at higher temperatures of 650-750° were thermal transformations of phenol observed, and in the gaseous reaction products the presence of hydrogen, methane, carbon monoxide, ethylene, acetylene, and butadiene has been established [4, 5]. Cawley [6] investigated the thermal conversions of phenol at 410, 430, and 450° in the absence of catalysts but under hydrogen pressure. Under certain conditions studied by us (under an initial hydrogen pressure of 100 atm), phenol underwent very insignificant transformation with the formation of benzene, the yield of which at 450° (after 2 hours) was only 1.8% of the initial phenol.

The investigation of the thermal conversion of phenol at high hydrogen pressures was carried out in a stainless steel reactor with a hydraulic closure and a volume of 120 ml. Forty g of phenol was charged to the reactor in each experiment. The phenol was first distilled in a fractionating column with an efficiency of 25 theoretical plates; the b. p. was 181.8-182.0°/760 . The initial hydrogen pressure was from 100 to 300 atm in the various experiments. The temperature of the experiment was held constant within the limits of ± 2° over a period of 3 hours. The working pressure was from 260 to 680 atm in the various experiments. At the conclusion of an experiment, the pressure was slowly reduced to atmospheric; the liquid product was collected in cooled traps. The reactor was then washed with ether, which was added to the product, and the combined liquids were dried over anhydrous sodium sulfate.

The reaction products were distilled in a fractionating column with an efficiency of 25 theoretical plates; the ether distilled first, and then the following fractions were collected: Fraction I, boiling range 60-83°; Fraction II, boiling range 83.1-175°; Fraction III, boiling range 175.1-183°. Fraction I contained primarily benzene; about 90% of this fraction boiled at 75-83°, $n_D^{20}$ 1.4863 – 1.4918. By a second distillation of the combined Fractions I from six experiments and subsequent chromatographic separation with silica gel, we were able to isolate a cyclohexane fraction with $n_D^{20}$ 1.4238; the somewhat low value of $n_D^{20}$ indicates the possible presence in this fraction of methylcyclopentane and hexane. Fraction II ($n_D^{20}$ 1.4948-1.4975) was an inter-plateau fraction (no indications of a plateau were observed on the distillation curve). Fraction III contained unchanged phenol. The high-boiling residue (boiling above 183°) was investigated separately.

In agreement with reference [6], the experiments carried out at 460° and an initial hydrogen pressure of 100 atm showed that the formation of benzene proceeds to a very slight extent under these conditions.

The results of the experiments carried out at 490°, $\tau$ = 3 hours, and various initial hydrogen pressures, are presented in Table 1. From a consideration of the data presented in this table, it follows that with an increase in the initial hydrogen pressure from 100 to 300 atm., the yield of the benzene fraction increases by almost a factor of 3.

As seen from Table 1, the deviations among the results of parallel experiments were small.

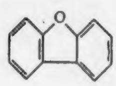
In order to determine whether this process is homogeneous, experiments were carried out at 490°, an initial hydrogen pressure of 100 atm, and a reaction time of 3 hours and with the addition to the reactor of shavings from the same stainless steel from which the reactor was constucted. The surface area of the shavings was

550 sq. cm; the area of the inside surface of the reactor was 330 sq. cm. The experiments showed that the surface of the metal and the ratio of the area to the reactor volume had no effect on the reaction rate:

| | | |
|---|---|---|
| S, sq. cm. | 330 | 880 |
| S/v, $cm^{-1}$ | 2.75 | 7.2 |
| Yield of Fraction I, wt. % of phenol charged | 8.5 | 8.8 |

Thus, this process is homogeneous.

After the distillations, the residues were combined and again distilled in the fractionating column. The fraction boiling at 183-185° (36 wt. %) was unchanged phenol; the fraction boiling at 185.1-215° (18 wt. %) consisted mainly of p-cresol, which was identified as p-toloxyacetic acid, m. p. 135.5-136°. After distillation from a column, the residue was distilled from a Claissen flask; this gave fractions boiling at 220-257° and 257-260° and also a solid residue, in which, after removal of the higher phenols (soluble in alkali), was established the presence of diphenylene oxide [dibenzofuran], m. p. 81-82° (from methyl alcohol). According to the literature [7], m. p. 82.8°.



Found %: C 85.75; H 4.90. $C_{12}H_8O$. Calculated %: C 85.72; H 4.76.

The fraction boiling at 220-257° contained biphenyl, m. p. 69-70; the melting sample containing pure biphenyl was unchanged. The fraction boiling at 257-260°, judging from the analytical data, apparently contained tetrahydrodiphenylene oxide [tetrahydrodibenzofuran].

Found %: C 83.54, 83.65; H 7.44, 7.45. $C_{12}H_{12}O$. Calculated %: C 83.66; H 6.97.

Table 2 presents the data on the composition of the gaseous reaction products.

The data of Table 2 (the last column in particular) indicate a considerable acceleration of the thermal decomposition of phenol with an increase in hydrogen pressure. The hydrocarbon composition of the gaseous reaction products within the pressure interval studied exhibited no essential change.

TABLE 1

Thermal Conversion of Phenol at High Hydrogen Pressures (t = 490°, $\tau$ = 3 hours)

| Initial hydrogen pressure in atm. | Working pressure in atm. | Yield of liquid products* (in wt. % of phenol charged) | | | | | |
|---|---|---|---|---|---|---|---|
| | | total | including | | | |
| | | | fraction I 60-83° | fraction II 83-175° | fraction III 175-183° | residue |
| 100 | 260 | 92.3 | 8.2 | 2.3 | 66.0 | 15.8 |
| 100 | 275 | 93.0 | 8.9 | 3.4 | 64.2 | 16.5 |
| 200 | 425 | 84.8 | 15.3 | 3.4 | 50.0 | 16.1 |
| 200 | 435 | 84.4 | 16.4 | 3.6 | 48.5 | 15.9 |
| 300 | 680 | 80.9 | 24.6 | 4.1 | 40.2 | 12.0 |
| 300 | 675 | 77.4 | 22.2 | 3.2 | 42.8 | 9.2 |

* Water-free.

The initial stage in the thermal decomposition of phenol is apparently the rupture of the O—H bond with the formation of a phenoxyl radical (cf. [8]). Therefore, the presence of diphenyl ether in the reaction products would be expected; however, we were unable to isolate this ether from the high-boiling fractions. We assumed that the diphenylene oxide could have been formed from diphenyl ether. This assumption was confirmed by an experiment carried out with diphenyl ether (32 g) at 490°, $\tau$ = 3 hours, and an initial hydrogen pressure of 200 atm. In the reaction products, along with unreacted diphenyl ether, was found 13.8 wt. %

benzene and 14.3 wt. % phenol. Diphenylene oxide was isolated from the high-boiling residue (6.1 wt. $\tau$); a mixed sample with diphenylene oxide obtained in the experiments with phenol (see above) melted without change of the melting point.

TABLE 2

Composition of the Gaseous Products in Volume Per Cent (experiments carried out at 490°, $\tau$ = 3 hours)

| Initial hydrogen pressure in atm. | $H_2$ | $CH_4$ | $C_2H_6$ | $C_3H_8$ | $C_4H_{10}$ | CO | CO, in mole % of phenol charged |
|---|---|---|---|---|---|---|---|
| 100 | 90.1 | 3.5 | 2.1 | 0.7 | 0.1 | 2.0 | 1.7 |
| 300 | 87.0 | 3.8 | 2.7 | 1.0 | 0.2 | 4.6 | 7.4 |

The investigation showed that thermal conversions of phenol at high hydrogen pressures lead to the formation of benzene as the major product. The presence of p-cresol, biphenyl, and diphenylene oxide, and also, apparently, tetrahydrodiphenylene oxide, was established in the high-boiling reaction products. It was shown that this process is homogeneous, and it was found that the yield of benzene, and of gaseous reaction products as well, increase considerably with an increase in the hydrogen pressure.

A comparison of the available literature data on the considerable thermal stability of phenol at 500° with the results of the present investigation permits the conclusion that this reaction proceeds by a radical-chain mechanism with the participation of hydrogen. The course of this mechanism can be represented as follows:

$$C_6H_5OH \rightarrow C_6H_5O^{\cdot} + H^{\cdot} \qquad (1)$$

$$H^{\cdot} + C_6H_5OH \rightarrow \dot{C}_6H_5 + H_2O \qquad (2)$$

$$\rightarrow CO + \text{Hydrocarbon radicals, } R \qquad (3)$$

$$\dot{C}_6H_5 + H_2 \rightarrow C_6H_6 + H \qquad (4)$$

$$R + H_2 \rightarrow RH + H^{\cdot} \qquad (5)$$

$$2\dot{C}_6H_5 \rightarrow C_6H_5 \cdot C_6H_5 \qquad (6)$$

$$C_6H_5 + C_6H_5O^{\cdot} \rightleftarrows (C_6H_5)_2O \rightarrow \underset{\text{Diphenylene oxide}}{(C_6H_4)_2O} + H_2 \qquad (7)$$

Reaction (1) is the first stage of the thermal decomposition of phenol; the interaction of the atomic hydrogen resulting from this reaction with a molecule of phenol (Reaction (2)) leads to the cleavage of the hydroxyl group from the benzene ring (similarly to the dealkylation of alkylbenzenes [9]). This process is accelerated by hydrogen pressure, since the latter determines the rate of Reaction (4) and the similar Reaction (5), in which molecular hydrogen participates, generating atomic hydrogen.

Our experiments showed that hydrogen pressure accelerates the decomposition of phenol with the formation of gaseous products. We assume that this process is also associated with the participation of atomic hydrogen, the addition of which to one of the carbon atoms of phenol leads to a decrease in the strength of the bond between this and the neighboring carbon atoms. Rupture of this C—C bond apparently leads to the formation of an unstable bi-radical which undergoes further decomposition to carbon monoxide and hydrocarbon radicals. The latter, in turn, can alkylate molecules of phenol with the formation of p-cresol, in particular, which was found in the reaction products.

As seen from the proposed scheme, Reactions (2)-(5) are chain-developing processes, and Reactions (6) and (7) are processes of chain termination; the higher the hydrogen pressure, the longer are the reaction chains. Thus, this scheme satisfactorily interprets our data on the composition of the products of the thermal conversion of phenol under high hydrogen pressure, and it also satisfactorily interprets our data on the effect of the magnitude of this pressure on the rate of the various stages of this process.

## LITERATURE CITED

[1] V. Ipatieff and N. Orlov, Ber. 60, 1966 (1927).

[2] A. Kling and D. Florentin, Bull. Soc. Chim. 41, 1341 (1927).

[3] D. Florentin, Compt. rend. 184, 855 (1927).

[4] A. Hagemann, Zs. angew. Chem. 14, 355 (1929).

[5] S. Ruhemann, Erdöl and Teer, 4, 629 (1928); 5, 10 (1929).

[6] C. M. Cawley, Fuel, 6, 217 (1935).

[7] A. F. Williams, Nature, 162, 925 (1948).

[8] N. N. Semenov, On Some Problems of Chemical Kinetics and Reactivity,* Izd. AN SSSR, 1954, p. 160.

[9] M. G. Gonikberg and V. E. Nikitenkov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, ** Proc. Acad. Sci. USSR, 102, 924 (1955).

N. D. Zelinskii Institute
of Organic Chemistry
Academy of Sciences USSR

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# REACTIONS OF 1,1'-DIMETHYLFERROCENE

Academician A. N. Nesmeianov, E. G. Perevalova,
Z. A. Beinoravichute and I. L. Malygina

The effect of substituents (acetyl, ethyl, p-nitrophenyl, carboxyl, and sulfonic acid groups) on the reactivity of the ferrocene nucleus has previously been noted [1-6].

The reactions of 1,1'-dimethylferrocene were investigated in the present work. Metalation and acylation of this compound were studied.

Attempts to metalate 1,1'-dimethylferrocene with n-butyllithium under conditions under which this reaction was carried out with ferrocene [7] were unsuccessful; dimethylferrocene was recovered unchanged. Methyl groups hinder the metalation of the ferrocene nucleus.

We used n-amylsodium as the metalating agent, this compound giving in the case of ferrocene, as shown by the present work, higher yields of 1,1'-ferrocenedicarboxylic acid than did phenylsodium. Moreover, the use of phenylsodium is less satisfactory owing to the formation of considerable amounts of benzoic acid [7].

Two courses of reaction are possible in the metalation of 1,1'-dimethylferrocene with n-amylsodium: substitution of a hydrogen of a methyl group or of a hydrogen of a cyclopentadienyl ring. By analogy to toluene, metalation of a methyl group would be expected. However, this possibility did not occur; metalation of 1,1'-dimethylferrocene with n-amylsodium occurred in the cyclopentadienyl ring. The main reaction product (52%) yield was a dimethyl ferrocenedicarboxylic acid with a decomposition temperature of 196-200°. Two other acids were isolated in very small amounts. One of these was an isomer of dimethylferrocene dicarboxylic acid, and the other was not investigated. All three acids gave solid dimethyl esters, and, consequently, none was di(carboxymethyl)ferrocene, which forms a liquid dimethyl ester [9]. The relative positions of the methyl and carboxyl groups have still not been established.

The acylation of dimethylferrocene was carried out with acetyl chloride in the presence of $AlCl_3$. The resulting dark red, viscous liquid was a mixture of acylation products and the original dimethylferrocene, which was readily removed chromatographically. The acylation products could not be separated by this method. On long standing, diacetyldimethylferrocene crystallized from the mixture, and this material was separated into two isomers by fractional crystallization. A comparison (of the melting points) with the diacetyldimethylferrocene isomers obtained by Rinehart and Motz [10] permits the assumption that our substances were stereoisomeric 1,1'-dimethyl-2,2'-diacetylferrocenes.

Monoacetylated dimethylferrocene was separated chromatographically from the liquid remaining after removal of the crystals. Oxidation of the same mixture with sodium hypochlorite gave dimethylferrocenetricarboxylic acid, which was identified as the trimethyl ester. Dimethyltriethylferrocene was isolated from the mixture after reduction with $LiAlH_4$.

The formation of dimethylferrocene tricarboxylic acid and dimethyltriethylferrocene shows that, in contrast to ferrocene, acylation of dimethylferrocene forms the triacylated product. This indicates considerable activation of the ferrocene nucleus by the methyl groups substitution reactions.

Furthermore, the initial mixture of products was subjected to catalytic hydrogenation under pressure in the presence of skeletal nickel [11] with the aim of establishing the structures of the acylation products from the structures of the resulting alkylcyclopentanes.

Distillation of the hydrogenation products in a column isolated four alkylcyclopentanes: methylcyclopentane, two methylethylcyclopentanes, and an alkylcyclopentane with a b. p. of 151-152.5°, which was probably the previously undescribed methyldiethylcyclopentane and which was formed from an acetyldimethylferrocene or a diacetyldimethylferrocene in which both acetyl groups were present on one cyclopentadienyl ring. The formation, during the acylation of dimethylferrocene, of such a diacetyldimethylferrocene in comparatively high yield is entirely possible as a consequence of the effect of the $CH_3$ groups, since even during the acylation of ferrocene itself, as is well known [5], a small amount of 1,2-diacetylferrocene is obtained.

## EXPERIMENTAL METHODS

### Metalation of Ferrocene with n-Amylsodium

To n-amylsodium, prepared from 11 g (0.48 g-atoms) of sodium and 25.5 g (0.24 mole) of n-$C_5H_{11}Cl$ in absolute octane [8], was added 11 g (0.059 mole) of ferrocene. The reaction mixture was stirred for 3.5 hours while heating at 100°, and was then allowed to stand overnight; the mixture was then poured onto solid $CO_2$. After 1 hour, 50 ml of methanol and 300 ml of water were added. The octane was separated. The aqueous layer was washed with ether. The ether solution was added to the octane solution. Distillation of the solvent yielded 3.2 g (29% of that introduced into the reaction) of ferrocene.

The aqueous layer was acidified with concentrated HCl. The precipitated 1,1'-ferrocenedicarboxylic acid was filtered and washed with hot water and hot benzene. The yield was 11.5 g (68% of theoretical, or practically quantitative if the unreacted ferrocene is taken into account). The dimethyl ester of this 1,1'-ferrocenedicarboxylic acid had a m. p. of 114-115°; a mixture with a known sample [12] showed no depression of the melting point.

Preparation of 1,1'-dimethylferrocene. 1,1'-Dimethylferrocene was prepared by the interaction of methylcyclopentadienyllithium* with $FeCl_3$ in ether solution. The yield was 37% of theoretical. M. p. 32.5-33° (from petroleum ether by cooling to −20°); $d_4^{35}$ 1.2349; $n_D^{35}$ 1.5900.

Metalation of 1,1'-dimethylferrocene with n-amylsodium. Metalation of 1,1'-dimethylferrocene (4.4 g; 0.0205 mole) was carried out as described for ferrocene. 1.2 g (27%) of the ferrocene was recovered unchanged.

The resulting mixture of acids was extracted with hot benzene and ether. The residue was dimethylferrocenedicarboxylic acid. The yield was 3 g (52% of theoretical). Decomposition temperature 196-200° (from alcohol).

Found %: C 55.96, 56.03; H 4.97, 5.04; Fe 18.99, 18.91. $C_{14}H_{14}O_4Fe$. Calculated %: C 55.62; H 4.63; Fe 18.54.

The dimethyl ester melted at 106-107° (from petroleum ether and methanol). Infrared spectrum (in vaseline oil):** 828; 854; 908; 940; 983; 1044; 1101; 1195; 1226; 1300; 1384; 1400; 1560; 1712 $cm^{-1}$.

Found %: C 58.41, 58.33; H 5.65, 5.58. $C_{16}H_{18}O_4Fe$. Calculated %: C 58.18; H 5.45.

From the benzene-ether extract was isolated 0.2 g of the isomeric dimethylferrocenedicarboxylic acid (washed with hot water and ether), decomposition temperature above 220° (from alcohol).

Found %: C 55.97, 56.12; H 4.86, 4.96; Fe 18.41, 18.33. $C_{14}H_{14}O_4Fe$. Calculated %: C 55.62; H 4.63; Fe 18.54.

Treatment of the acid with diazomethane gave the ester, m. p. 81-82°. Infrared spectrum (in vaseline oil): 832; 851; 906; 942; 982; 1044; 1099; 1151; 1193; 1220; 1308; 1392; 1460; 1560; 1712 $cm^{-1}$.

From the ether, with which the acid was washed, was isolated a very small amount of an acid with a decomposition temperature of 132-140°; the methyl ester melted at 75-76°.

Acylation of 1,1'-dimethylferrocene. To a mixture of 13.3 g (0.1 mole) of $AlCl_3$, 40 ml of $CS_2$, and 8 ml (0.1 mole) of $CH_3COCl$ was added, over a period of 2 hours with vigorous stirring in an atmosphere of

* The authors wish to thank N. I. Shuikin and T. I. Naryshkina for the gift of the methylcyclopentadiene.

** The i. r. spectrum was taken by L. A. Kazitsina and B. V. Lokshin.

nitrogen,* 8 g (0.034 mole) of 1,1'-dimethylferrocene dissolved in 40 ml of $CS_2$. Stirring was continued for 20 minutes at room temperature and 1.5 hours with heating just barely to boiling. The reaction mixture was then cooled with ice water. The $CS_2$ layer, which became almost colorless, was decanted, and the residue was treated with cooled 1% HCl and then extracted with ether. From the ether extract was obtained 8.4 g of a mixture of acylation products and unreacted 1,1'-dimethylferrocene; the mixture was dissolved in a mixture of petroleum ether and benzene (1:3) and resolved chromatographically over $Al_2O_3$. There were three bands in the column. 1.3 g (16%) of the original 1,1'-dimethylferrocene was eluted with petroleum ether from the lower, yellow band. The middle, crimson-colored band was eluted with absolute benzene. This gave 0.3 g of crimson material which, in contrast to the acylated dimethylferrocene, was not soluble in concentrated HCl. This material was not investigated further.

The last band (dark red color) was eluted with methanol. This gave 5.9 g of a liquid mixture of acylated dimethylferrocenes in which, by the different methods described below, were detected a monoacetyldimethylferrocene, three diacetyldimethylferrocenes, and a triacetyldimethylferrocene.

Diacetyldimethylferrocene. 0.5 g of an orange-red crystalline material, which was purified chromatographically over $Al_2O_3$, separated from 5.9 g of the mixture of dimethylferrocene acylation products when the latter stood for 1 month at a temperature of from $-10$ to $-12°$, m. p. 93-94°. Diacetyldimethylferrocene with a m. p. of 87.5-88.5° was obtained by recrystallization from methanol (precipitated on standing for a day at 0-5°).

Found %: C 64.09, 64.14; H 6.00, 6.11. $C_{16}H_{18}O_2Fe$. Calculated %: C 64.45; H 6.09.

Diacetyldimethylferrocene with a m. p. of 98.5-99.5° was isolated from the mother liquor.

Found %: C 64.63, 64.66; H 6.17, 6.14; Fe 18.72. $C_{16}H_{18}O_2Fe$. Calculated %: C 64.45; H 6.09; Fe 18.73.

These substances are probably stereoisomeric 1,1'-dimethyl-2,2'-diacetylferrocenes, for which Rinehart and Motz [10] reported melting points of 84-86° and 102-103°.

Monoacetyldimethylferrocene. The mixture of acylation products remaining after separation of the diacetyldimethylferrocene was dissolved in a mixture of petroleum ether and benzene (1:1) and passed through a column packed with $Al_2O_3$. The fraction eluted with $CH_3OH$ was again chromatographed. Monoacetyldimethylferrocene was obtained as a reddish brown oil.

Found %: C 65.47, 65.34; H 6.26, 6.54. $C_{14}H_{16}OFe$. Calculated %: C 65.61; H 6.29.

The semicarbazone of the monoacetyldimethylferrocene decomposed at 147-150° (reprecipitated from $C_2H_5OH$-water).

Found %: C 57.29, 57.08; H 6.03, 6.03; Fe 18.13, 18.00. $C_{15}H_{19}N_3OFe$. Calculated %: C 57.52; H 6.12; Fe 17.83.

1,1'-Dimethylferrocenetricarboxylic acid. One g of the mixture of acylation products remaining after separation of the diacetyldimethylferrocene was dissolved in 5 ml of methanol and oxidized with sodium hypochlorite [5]. 0.35 g of the acylation product was recovered. 0.06 g of dimethylferrocene tricarboxylic acid (washed with hot benzene) was isolated, the trimethyl ester of which melted at 83-84° (from benzene and from alcohol).

Found %: C 55.60, 55.62; H 5.19, 5.20. $C_{18}H_{20}O_6Fe$. Calculated %: C 55.69; H 5.19.

1,1'-Dimethyltriethylferrocene. 1.5 g of the acylated dimethylferrocene (after separation of the diacetyldimethylferrocene) was reduced with $LiAlH_4$ [7]. From the resulting mixture was chromatographically separated dimethyltriethylferrocene — a reddish brown, oily substance. It altered rapidly in air.

*When the reaction is carried out in air, there is sometimes formed a dark, powder material which contains halogen and which is not soluble in organic solvents or acids.

Found %: C 72.33, 72.19; H 8.45, 8.55; Fe 19.11, 18.54. $C_{18}H_{28}Fe$. Calculated %: C 72.49; H 8.78; Fe 18.73.

Hydrogenation [11]. Sixteen g of acylated dimethylferrocene (unreacted dimethylferrocene removed chromatographically), 60 ml of $C_2H_5OH$, and 4 ml of skeletal Ni were charged to an autoclave. The initial $H_2$ pressure was 95 atm. The hydrogenation was carried out for 1 hour at 110-120°, 4 hours at 230°, and 2 hours at 250-280°. The reaction products were extracted with ether. The ether solution was carefully washed with water to remove the alcohol, and dried. Distillation of the ether and fractionation of the products was carried out in a column of 35 theoretical plates. Decalin was used as a chaser.

The following were isolated: methylcyclopentane (2 ml), b. p. 69.5-71.5°/750 mm, $n_D^{20}$ 1.4100, $d_4^{20}$ 0.7496; and two methylethylcyclopentanes (about 0.9 ml), b. p. 120-121°/750 mm, $n_D^{20}$ 1.4218; $d_4^{20}$ 0.7681, and b. p. 125-125.5°, $n_D^{20}$ 1.4261.

Judging from the physical constants [13], the lower boiling methylethylcyclopentane could have been the trans-1,2- or the cis-1,3-isomer. The second methylethylcyclopentane was probably the cis-1,2-isomer [13].

In addition, there was obtained 1.0 ml of an alkylcyclopentane with a b. p. of 151-152.5°/750 mm $n_D^{20}$ 1.4428; this was probably methyldiethylcyclopentane, previously undescribed in the literature.

Found %: C 85.68, 85.84; H 14.34, 14.37. $C_{10}H_{20}$. Calculated %: C 85.71; H 14.38.

## LITERATURE CITED


[1] A. N. Nesmeianov and E. G. Perevalova, et al., Bull. Acad. Sci. USSR, Div. Chem. Sci., 1957, 638.*

[2] A. N. Nesmeianov and N. A. Vol'kenau, Proc. Acad. Sci. USSR, 111, 605 (1956).*

[3] A. N. Nesmeianov, E. G. Perevalova, S. S. Churanov and O. A. Nesmeianova, Proc. Acad. Sci. USSR, 119, No. 5 (1958).*

[4] A. N. Nesmeianov and O. A. Reutov, Proc. Acad. Sci. USSR, 115, 518 (1957).*

[5] I. H. Richards and T. J. Curphey, Chem. and Ind. 1956, 1456.

[6] P. L. Pauson, Quart. Rev. 9, 391 (1955).

[7] A. N. Nesmeianov, E. G. Perevalova and Z. A. Beinoravichute, Proc. Acad. Sci. USSR, 112, 439 (1957).*

[8] K. A. Kocheshkov and T. V. Talalaeva, Synthetic Methods In the Field of Organometallic Compounds, Vol. I, Izd. AN SSSR, 1949, pp. 165, 184.**

[9] K. L. Rinehart, Jr. R. J. Curby, Jr., and P. E. Sokol, J. Am. Chem. Soc. 79, 3420 (1957).

[10] K. L. Rinehart, Jr. K. L. Motz, Chem. and Ind. 1957, 1150.

[11] A. N. Nesmeianov and E. G. Perevalova, et al., Bull. Acad. Sci. USSR, Div. Chem. Sci., 1956, 739.*

[12] R. B. Woodward, M. Rosenblum and M. C. Whiting, J. Am. Chem. Soc. 74, 3458 (1952).

[13] Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Pittsburgh, Pennsylvania, 1953, p. 47.


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# FUNCTIONAL DERIVATIVES OF 1,1'-FERROCENEDICARBOXYLIC ACID

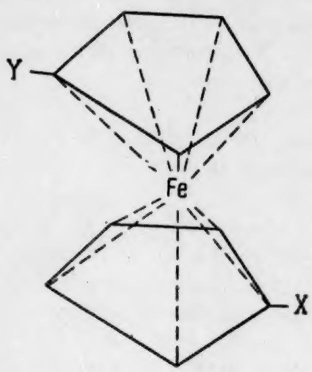
Nik. A. Nesmeianov and O. A. Reutov

(Presented by Academician A. N. Nesmeianov, February 11, 1958)

1,1'-Ferrocenedicarboxylic acid was prepared by Woodward and co-workers in 1952 [1]; however, up to now, no derivatives of this acid have been known with the exception of the dimethyl ester (II) (see Table 1) [1] and the monomethyl ester (II) [2]. In the present work, a series of new derivatives of this acid were prepared.

TABLE 1

| | X | Y |
|---|---|---|
| I | —COOH | COOH |
| II | $—COOCH_3$ | $—COOCH_3$ |
| III | —COOH | $—COOCH_3$ |
| IV | —COCl | —COCl |
| V | $—CONH_2$ | $—CONH_2$ |
| VI | $—COOCH_3$ | $—CONH_2$ |
| VII | —COOH | $—CONH_2$ |
| VIII | —COOH | —CN |
| IX | —CN | —CN |
| X | —H | —CN |




The chloride of 1,1'-ferrocenedicarboxylic acid (IV) was prepared in 30% yield by reacting 0.025 mole of this acid with 0.05 mole of phosphorus trichloride in 40 ml of benzene 3 hours in the cold and subsequently heating the reaction mixture at 50-60° for 2 hours. It was a red substance which crystallized from petroleum ether and which was readily soluble in organic solvents. M. p. 92-93°.

Found %: C 46.83, 46.87; H 2.68, 2.65; Fe 18.07, 17.94. $C_{12}H_8FeO_2Cl_2$. Calculated %: C 46.35; H 2.59; Fe 17.96.

Hydrolysis of the pure acid chloride (IV) proceeds comparatively slowly. Thus, it is hydrolyzed by a 20% solution of soda only on heating or on long standing in the cold; in this respect, it is similar to the chlorides of aromatic acids.

The amide (V) of 1,1'-ferrocenedicarboxylic acid was prepared from the acid chloride in a yield close to quantitative; the amide is a yellow compound, insoluble in nonpolar and difficultly soluble in polar solvents. It can be recrystallized from water. It decomposes in the temperature interval 270-275°.

Found %: C 53.02, 53.10; H 4.25, 4.31; F 20.33, 20.42; N 13.11, 12.91. $C_{12}H_{12}FeO_2N_2$. Calculated %: C 52.98; H 4.44; F 20.53; N 13.21.

Heating the monomethyl ester of 1,1'-ferrocenedicarboxylic acid (III) for 2 hours in phosphorus trichloride gave the corresponding acid chloride; this compound was not isolated, and, after removal of the solvent, it was treated in the cold with a 25% solution of ammonia. The resulting methyl ester of 1-carbamidoferrocene-1'-carboxylic acid [methyl ester of 1-carbamoyl-1'-ferrocenecarboxylic acid], a yellow powder, was recrystallized from toluene and from methanol. The yield was 60%. The material was readily soluble in acetone, alcohol, chloroform, and hydrochloric acid. M. p. 143.5-145°.

Found %: C 54.85, 54.94; H 4.50, 4.60; Fe 19.51, 19.29; N 5.09, 5.12. $C_{13}H_{13}FeO_3N$. Calculated %: C 54.40; H 4.56; Fe 19.45; N 4.88.

This ester was hydrolyzed with excess 10% NaOH by heating on a water bath for 15 minutes. The 1-carbamidoferrocene-1'-carboxylic acid (VIII) [1-carbamoyl-1'-ferrocenecarboxylic acid] was reminiscent of the above-described amide of 1,1'-ferrocenedicarboxylic acid (V) with respect to solubility. It gradually decomposed when heated above 200°. It could be recrystallized from acetic acid and from methanol.

Found %: C 52.97, 53.08; H 3.94, 4.00; Fe 20.56, 20.83; N 5.37, 5.27. $C_{12}H_{11}FeO_3N$. Calculated %: C 52.78; H 4.05; Fe 20.45; N 5.13.

It was found that the above-described amides (V) and (VII), and also the amide of ferrocenecarboxylic acid * could be converted into the corresponding nitriles by heating with acetic anhydride.

Heating 1-carbamidoferrocene-1'-carboxylic acid (VII) with acetic anhydride at 140° for 20 minutes gave a 55% yield of 1-cyano-1'-ferrocenecarboxylic acid (VIII), a yellow substance with a m. p. of 179-180° (with decomposition) which was more soluble in polar than in nonpolar solvents. It could be recrystallized from toluene and from methanol.

Found %: C 56.56, 56.64; H 3.65, 3.76; Fe 21.88, 21.86; N 5.86, 6.07. $C_{12}H_9FeO_2N$. Calculated %: C 56.52; H 3.56; Fe 21.90; N 5.49.

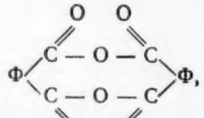
The nitrile of 1,1'-ferrocenedicarboxylic acid (IX) was prepared by heating the amide of this acid (V) with acetic anhydride (10 ml of acetic anhydride per gram of amide) at 100° for 6 hours, and subsequently heating the reaction mixture in a sealed tube at 170°. The yield was 30%. M. p. 166-167.5° (with decomposition) in a sealed capillary. The material could be recrystallized from methanol and from toluene.

Found %: C 61.17, 60.96; H 3.55, 3.49; Fe 23.73, 23.56; N 11.80, 11.73. $C_{12}H_8FeN_2$. Calculated %: C 61.06; H 3.37; Fe 23.66; N 11.87.

Heating the amide of ferrocenecarboxylic acid with acetic anhydride at 140° for 40 minutes gave the nitrile of this acid (X), and 20% of the original material was recovered. M. p. (X) 106.5-107.5°; literature value 103-104°. **

Found %: C 62.74, 62.87; H 4.10, 4.25; Fe 26.21, 26.07; N 6.60, 6.77. $C_{11}H_9FeN$. Calculated %: C 62.61; H 4.29; Fe 26.47; N 6.64.

By the action of pyridine on acid chloride (IV) in chloroform in the presence of water, the elements of HCl were split out of two molecules of the acid chloride and two molecules of water with the formation of the anhydride of 1,1'-ferrocenedicarboxylic acid (XI).***



where $\Phi = -C_5H_4-Fe-C_5H_4-$

(XI)

* Described by Arimoto and Haven [3].

** This nitrile was prepared by the American authors by dehydration of the oxime of the corresponding aldehyde [4].

*** V. K. Plakunov took part in the preparation of anhydride (XI).

The yield amounted to as much as 65% if the reaction was carried out as follows. To a solution of 0.01 mole of acid chloride (IV) in 15 ml of chloroform was added dropwise and with stirring 0.05 mole of pyridine in chloroform; 1.2 ml of water was added immediately, and the mixture was agitated and then allowed to stand for 12 hours. The chloroform solution was then washed with 2% hydrochloric acid, a soda solution, and water, and dried over calcium chloride. The solvent was removed under vacuum, and the residue was washed with ether; the resulting material was a yellow powder, difficultly soluble in the majority of organic solvents, except chloroform; it decomposed in the range of 230-240° (after recrystallization fron nitromethane).

Found %: C 55.92, 55.75; H 3.25, 3.37; Fe 21.60, 21.30. $C_{12}H_8FeO_3$. Calculated %: C 56.28; H 3.15; Fe 21.80.

The molecular weight (cryoscopic in dioxane) was: found 556, 528, calculated 512.

Another proof of the dimeric formula given above for the anhydride is its reaction with aqueous ammonia. This reaction gave three products: the amide of 1,1'-ferrocenedicarboxylic acid (V), the ammonium salt of this acid, and 1-carbamidoferrocene-1'-carboxylic acid (VII) (approximately in the ratios 1 : 1 : 2, respectively). The formation of only the latter product would be expected from the monomeric anhydride. The acids formed in this reaction were separated and identified as their methyl esters. Anhydride (XI) hydrolyzes on heating with dilute alkali, and lengthy heating with methanol in the presence of hydrochloric acid gives the methyl ester of 1,1'-ferrocenedicarboxylic acid (II).

In passing, we characterized certain salts of 1,1'-ferrocenedicarboxylic acid. The sodium, potassium, and lithium salts of this acid are readily soluble in water and difficultly soluble in strong alkalies, and, owing to this, they can be obtained in the solid form by treatment of the dry acid with concentrated alkalies. The crystals of the salts can be washed on the filter with a small amount of methanol to remove the alkali.

The yellow-green copper (cupric) salt of acid (I) is practically insoluble in water. When 0.01 M aqueous solutions of lead acetate and the sodium salt of acid (I) are mixed, the lead salt of this acid precipitates. The barium and magnesium salts of this acid are more soluble in water. These salts precipitate when cold saturated solutions of the chlorides of these metals are mixed with a 0.05 M solution of the sodium salt of acid (I).

In conformity with the aromatic nature of ferrocene, it was found that the radical $-CCl_3$, formed by heating trichloroacetic acid in the presence of cupric chloride, is capable of replacing one of the hydrogens of ferrocene. This reaction was previously known only for such compounds as naphthalene and xylene [5]. The decomposition of trichloroacetic acid was carried out in a saturated solution of an equimolar amount of ferrocene in nitrobenzene at 120-130°. The trichloroacetic acid was added portion-wise, together with catalytic amounts of anhydrous cupric chloride and pyridine. At the conclusion of the reaction, the reaction mixture was heated with 10% NaOH, and ferrocenecarboxylic acid was separated from the alkaline extract. After recrystallization from toluene and methanol, the yield of acid was 6%; the melting point was 220-222° (with decomposition) in a sealed capillary. According to the literature, this acid decomposes above 200° [6, 7].

Found %: C 57.74, 57.62; H 4.50, 4.41; Fe 24.08, 24.12. $C_{11}H_{10}O_2Fe$. Calculated %: C 57.43; H 4.39; Fe 24.28.

Treatment of this acid with diazomethane gave the methyl ester with a m. p. of 68-69°, which corresponds to the literature value [6].

Though the conditions of the decomposition of trichloroacetic acid in a mixture with ferrocene were varied, no products of the double trichloromethylation of ferrocene were detected.

## LITERATURE CITED

[1] R. B. Woodward, M. Rosenblum and M. G. Whiting, J. Am. Chem. Soc. 74, 3458 (1952).

[2] Nik. A. Nesmeianov and O. A. Reutov, Proc. Acad. Sci. USSR, 115, 518 (1957).*

[3] F. S. Arimoto and A. C. Haven, J. Am. Chem. Soc. 77, 6295 (1955).

*Original Russian pagination. See C. B. Translation.

[4] P. J. Graham, et al., J. Am. Chem. Soc. 79, 3416 (1957).

[5] A. N. Nesmeianov, K. A. Pecherskaia and G. Ia. Ukretskaia, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1949, 607.

[6] A. N. Nesmeianov, E. G. Perevalova, R. V. Golovnia and O. A. Nesmeianova, Proc. Acad. Sci. USSR, 97, 459 (1954).

[7] R. Benkeser, D. Goggin and G. Schroll, J. Am. Chem. Soc. 76, 4025 (1954).

M. V. Lomonosov Moscow
State University

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## SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

| | |
|---|---|
| FIAN | Phys. Inst. Acad. Sci. USSR. |
| GDI | Water Power Inst. |
| GITI | State Sci.-Tech. Press |
| GITTL | State Tech. and Theor. Lit. Press |
| GONTI | State United Sci.-Tech. Press |
| Gosenergoizdat | State Power Press |
| Goskhimizdat | State Chem. Press |
| GOST | All-Union State Standard |
| GTTI | State Tech. and Theor. Lit. Press |
| IL | Foreign Lit. Press |
| ISN (Izd. Sov. Nauk) | Soviet Science Press |
| Izd. AN SSSR | Acad. Sci. USSR Press |
| Izd. MGU | Moscow State Univ. Press |
| LEIIZhT | Leningrad Power Inst. of Railroad Engineering |
| LET | Leningrad Elec. Engr. School |
| LETI | Leningrad Electrotechnical Inst. |
| LETIIZhT | Leningrad Electrical Engineering Research Inst. of Railroad Engr. |
| Mashgiz | State Sci.-Tech. Press for Machine Construction Lit. |
| MEP | Ministry of Electrical Industry |
| MES | Ministry of Electrical Power Plants |
| MESEP | Ministry of Electrical Power Plants and the Electrical Industry |
| MGU | Moscow State Univ. |
| MKhTI | Moscow Inst. Chem. Tech. |
| MOPI | Moscow Regional Pedagogical Inst. |
| MSP | Ministry of Industrial Construction |
| NII ZVUKSZAPIOI | Scientific Research Inst. of Sound Recording |
| NIKFI | Sci. Inst. of Modern Motion Picture Photography |
| ONTI | United Sci.-Tech. Press |
| OTI | Division of Technical Information |
| OTN | Div. Tech. Sci. |
| Stroiizdat | Construction Press |
| TOE | Association of Power Engineers |
| TsKTI | Central Research Inst. for Boilers and Turbines |
| TsNIEL | Central Scientific Research Elec. Engr. Lab. |
| TsNIEL-MES | Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants |
| TsVTI | Central Office of Economic Information |
| UF | Ural Branch |
| VIESKh | All-Union Inst. of Rural Elec. Power Stations |
| VNIIM | All-Union Scientific Research Inst. of Meteorology |
| VNIIZhDT | All-Union Scientific Research Inst. of Railroad Engineering |
| VTI | All-Union Thermotech. Inst. |
| VZEI | All-Union Power Correspondence Inst. |

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.